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THERMOELECTRIC TEMPERATURE SCALES

By Wm. F. Roeser

ABSTRACT

The International Temperature Scale, adopted in 1927 by the Seventh General Conference of Weights and Measures, representing 31 nations, is the fourth thermoelectric temperature scale used by the Bureau of Standards since 1912. In putting this scale into use it was necessary for the Bureau of Standards to replace all of the fixed points used previous to 1926 by new fixed points specified in the International Temperature Scale. It is the purpose of this work to determine how much change this has caused in the temperature scale and to make available comparisons between the various scales used by the Bureau of Standards at different times since 1912.

The difference between four thermoelectric temperature scales based upon (1) Sb, Ag, and Au; (2) Zn, Sb, Ag, and Au; (3) Zn, Al, and Cu; and (4) Zn, Sb, and Cu as calibration points have been determined. The maximum difference between (1) and (2) was found to be 0.1° C., between (1) and (3) 0.2° C., and between (1) and (4) 0.3° C. in the temperature range 660° to 1,063° C.

The freezing point of the copper-silver eutectic alloy, 71.9 per cent silver and 28.1 per cent copper, on the International Temperature Scale was found to be 779.4° C. ±0.1° C.

The difference between the freezing points of gold and copper was found to be 20.0° C. ±0.1° C.

Methods used at the Bureau of Standards in realizing the International Temperature Scale in the range 660° to 1,063° C. are described in detail.

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I. INTRODUCTION

The International Temperature Scale [1] adopted in 1927 defines temperatures in the range 660° to 1,063° C. as follows:

* * * The temperature t is deduced from the electromotive force e of a standard platinum *v.* platinum-rhodium thermocouple, one junction of which is kept at constant temperature of 0° C., while the other is at the temperature t defined by the formula

$$e=a+bt+ct^2$$

The constants a, b, and c are to be determined by calibration at the freezing point of antimony and at the silver and gold points.

[1] Proc. Seventh General Conference of Weights and Measures, 1927, p. 56. Text in Annex IV, p. 94. G. K. Burgess, B. S. Jour. Research, 1, p. 635; October, 1928.

Previous to the adoption of the International Temperature Scale by the national laboratories several other thermoelectric temperature scales had been extensively used, and much data had been published in terms of these various scales. So far no data are available which give accurately the differences between all of these various scales. Henning and Otto [2] have published the difference between the average calibrations of two thermocouples, which give a comparison between the thermoelectric temperature scale previously used by the Physikalisch-Technische Reichsanstalt and the International Temperature Scale. Since it is important to be able to compare results expressed in terms of any one of the scales with those expressed in terms of another scale, it is highly desirable that the differences between some of the other scales be accurately determined.

The International Temperature Scale is intended to reproduce as closely as can be done with present knowledge the Centigrade Thermodynamic Temperature Scale, on which the temperature of melting ice and of condensing water vapor, both under the pressure of one standard atmosphere, are numbered 0° and 100°, respectively. This scale would be exactly realized with an ideal gas in a perfect gas thermometer and may be closely realized with the more permanent of the actual gases. From the departure of certain properties of these gases from those of an ideal gas it is possible to deduce the amount of the departure of the temperature scales, defined by their use, from the thermodynamic scale.

The gas thermometer is not a convenient instrument for ordinary use, and except under the most favorable conditions has not yielded results of high accuracy. The results of the best gas thermometer determinations have been made permanently available in the form of values for the temperatures of certain thermometric fixed points, such as freezing or boiling points of pure substances. The values accepted for such points depend not upon individual observations with one instrument nor upon a series of such observations, but are the weighted means of all published data, and are therefore more reliable than any single determination or series of determinations. Temperatures up to the melting point of palladium have thus been determined with the gas thermometer. These thermometric fixed points can be used in defining practical temperature scales with the aid of convenient interpolation instruments, such as thermocouples or resistance thermometers. The precision attainable with these thermometers calibrated at suitable fixed points is far greater than has been attained with the gas thermometer, except at very low temperatures

[2] Henning and Otto, Zeit. f. Phys. 49, p. 742; 1928.

II. PRACTICAL TEMPERATURE SCALES

The definition of any practical temperature scale must specify (1) values for the reproducible temperatures at which instruments are to be calibrated, (2) the type of instruments to be used in the realization of the temperature scale, and (3) the form of the equation to be used for interpolating between or extrapolating beyond the calibration points.

Prior to the adoption of the International Temperature Scale the platinum to platinum-10 per cent rhodium thermocouple was almost universally used for defining temperature scales in the range 450° to 1,100° C., and the equations used were either the quadratic $E=a+bt+ct^2$ or the cubic $E=a+bt+ct^2+dt^3$, depending upon the number of calibration points.

Thermoelectric temperature scales which have been extensively used for defining temperatures in the range 450° to 1,100° C. are described below. In all cases the platinum to platinum-10 per cent rhodium thermocouple has been the instrument used in the realization of these scales.

The scale based upon the work of Holborn and Day [3] was defined by the thermocouple calibrated at the freezing point of zinc (419.0°C.) antimony (630.6° C.) and copper (1,084.1° C.) with the quadratic equation for interpolating. This scale with the above values was almost universally used from 1900 to 1909. The work of Waidner and Burgess [4] in 1909 and of Day and Sosman [5] in 1910 and 1912 necessitated a readjustment of the above values, and in 1912 the Bureau of Standards redefined its scale, retaining the quadratic equation but assigning values determined with the resistance thermometer to the freezing points of the zinc and antimony in use, while the freezing point of copper was taken as 1,083.0° C. Here for convenience this 1912 scale of the Bureau of Standards, which was used from, 1912 to 1916, will be designated as the Zn, Sb, and Cu temperature scale.

The temperature scale proposed by Sosman [6] and revised by Adams,[7] both of the Geophysical Laboratory, was realized by using a standard reference table, which gives the average temperature-emf relation for several of the thermocouples used by Day and Sosman. A deviation curve is determined for any other thermocouple by calibration at several, preferably three or more of the fixed points, the values for which were determined by Day and Sosman,

[3] Holborn and Day, Am. J. Sci., **10**, p. 17; 1900.
[4] Waidner and Burgess, B. S. Bull., **6**, No. 2, p. 149; 1909.
[5] Day and Sosman, Car. Inst. of Wash. Pub. No. 157; 1911. Am. J. Sci. **33**, p. 517; 1912.
[6] R. B. Sosman, Am. J. Sci. (4), **30**, p. 7; 1910.
[7] L. H. Adams, J. Am. Chem. Soc., **36**, p. 65; 1914.

and then plotting the difference between the observed emf and the emf from the reference table against the observed emf of the thermocouple. This scale, although very convenient, is not completely defined in that it does not specify the particular calibration points to be used. Because of this lack of definition it was not feasible to make comparison between this scale and others described here.

In 1916 the Physikalisch-Technische Reichsanstalt adopted a temperature scale in which the thermocouple was calibrated at the freezing points of cadmium (320.9° C.), antimony (630° C.), gold (1,063° C.), and palladium (1,557° C.) and a cubic equation was used for interpolating. No comparison of this scale with the other scales described will be made here, since this would have necessitated calibration at the freezing point of palladium, which was considered inadvisable in the case of thermocouples to be used for precise measurements at lower temperatures.

The temperature scale adopted by the Bureau of Standards in 1916 was defined by the thermocouple calibrated at the freezing points of zinc and aluminum (the values for which were determined by the resistance thermometer) and at the copper point (1,083.0° C.) and the quadratic equation was retained for interpolating. This scale was used by the Bureau of Standards from 1916 to 1926 and will be designated as the Zn, Al, and Cu temperature scale.

The temperature scale which was adopted by the Physikalisch-Technische Reichsanstalt in 1924 and by the Bureau of Standards in 1926 was defined by the thermocouple calibrated at the freezing points of zinc and antimony (the values for which were determined by the resistance thermometer) and at the silver point (960.5° C.) and the gold point (1,063.0° C.) with the cubic equation for interpolating. This scale will be designated as the Zn, Sb, Ag, and Au temperature scale.

In 1927 the Seventh General Conference of Weights and Measures, representing 31 nations, unanimously adopted the International Temperature Scale referred to above. This scale in so far as the temperature range 660° to 1,063° C. is concerned is merely the Zn, Sb, Ag, and Au scale with the zinc point omitted. In putting this scale into use it has been necessary for the Bureau of Standards to abandon all of the three fixed points used previous to 1926 and to substitute three other points. It is the purpose of this work to determine how much change this has caused in the temperature scale, and to make available comparisons between some of the various scales used at different times by the Bureau of Standards.

A list of freezing points available for the calibration of thermocouples and used in defining various temperature scales in the range 400° to 1,100° C. is given in Table 1.

TABLE 1.—*Freezing points available for calibration of thermocouples*

	°C.
1. Temperature of freezing zinc	419. 47
2. Temperature of freezing antimony	630. 52
3. Temperature of freezing aluminum	659. 23
4. Temperature of freezing silver	960. 5
5. Temperature of freezing gold	1, 063. 0
6. Temperature of freezing copper in a reducing atmosphere	1, 083

The temperatures given are those corresponding to a pressure of one standard atmosphere. The values for the freezing points of zinc, antimony, and aluminum are for the particular samples employed by the Bureau of Standards and have been determined with the platinum resistance thermometer, which defines the International Temperature Scale up to 660° C. The values given for the freezing points of silver and gold, basic fixed points, and for the freezing point of copper, a secondary point, are those assigned to the various points by international agreement in the International Temperature Scale.

It would be desirable to have a suitable fixed point between the freezing point of aluminum (659.23° C.) and the freezing point of silver (960.5° C.) which could be used as a secondary point for determining the reproducibility of the various temperature scales. Such a point would also be useful in the calibration of optical pyrometers in this temperature range. The freezing point of the eutectic alloy of silver and copper, 71.9 per cent Ag, 28.1 per cent Cu, by weight, has been used to some extent at the Bureau of Standards for the above purposes. This material behaves very much as an element in so far as freezing and melting are concerned. We have no record of gas thermometer measurements on the freezing point of this alloy, but the value 779° C. was assigned to this point by the bureau as a result of thermocouple measurements. It is also the purpose of this work to determine the freezing point of the copper-silver eutectic alloy on the International Temperature Scale to an accuracy of 0.1° C.

III. APPARATUS AND PROCEDURE

The thermocouples used in this investigation were taken from the thermocouple stock prepared by the Bureau of Standards. Both the platinum and platinum-rhodium were spectroscopically pure. The composition of the alloy wire was as nearly 10 per cent rhodium as can be determined by present methods of analysis. Both of the couples were electrically annealed for six hours at 1,500° C. before being used. These two thermocouples will be designated E_2 and E_3.

Table 2 gives the data available on the purity and origin of the freezing point samples employed.

TABLE 2.—*Freezing point samples*

Sample	Purity	Prepared by—
	Per cent	
Zinc	99.993	New Jersey Zinc Co.
Antimony	99.9+	C. A. F. Kahlbaum, Berlin.
Aluminum	99.81	Aluminum Co. of America.
Silver	[1] 99.9+	U. S. Bureau of the Mint.
Gold	[2] 99.99	Do.
Copper	99.987	Raritan Copper Co.
Ag–Cu eutectic	[3]	Bureau of Standards.

[1] Proof silver. [2] Proof gold. [3] Silver, 71.9 per cent; copper, 28.1 per cent.

All of the above materials were used in Acheson graphite crucibles 15 cm deep and 3 cm inside diameter with a wall 9 mm thick. All of the materials, with the exception of gold, were covered with flake graphite to prevent oxidation during use.

A separate electric furnace was used for each metal or alloy. All the furnaces are of identical design. Figure 1 shows the construction of the furnaces and the method of supporting and protecting the freezing point sample. The graphite crucible *H* containing the metal *M* and the pyrometer protecting tube *A* is supported by silocel cylinders *L*. The heater tube *B* is of alundum (R. A. 98); length, 38 cm; inside diameter, 5.1 cm; and wall thickness, 1.0 cm. The heater tube is wound on the outside with B. & S. gage No. 6 "chromel A" wire *C*, which is embedded in alundum cement. Two Acheson graphite diaphrams *D* are placed above the crucible in order to minimize the oxidation and to promote temperature uniformity within the metal. The furnace shell *I* is made of sheet steel rolled and riveted into a cylinder. The space *O* between the heating element and furnace shell is filled with silocel powder. The annular space between the alundum tube and furnace shell is closed at the top with clay-graphite plate *P*. The hot junction of a chromel-alumel thermocouple *E* is embedded in the heating element and the wires brought through the shell to binding posts. This thermocouple provides a convenient means of indicating or controlling the temperature of the furnaces. All the lead wires are insulated from the furnace shell with bakelite bushings *J*.

The wires of the thermocouple to be calibrated were threaded through the two 1 mm holes in a porcelain insulating tube, 50 cm long and 4 mm in diameter. This insulating tube was placed inside a glazed porcelain tube 50 cm long and 5 mm inside diameter with a wall 1 mm thick. Each protection tube and insulating tube before use was heated in a furnace to a temperature above that at which measurements were to be made in order to burn out foreign materials which might have contaminated the thermocouples. A different protection tube was used for each freezing point sample.

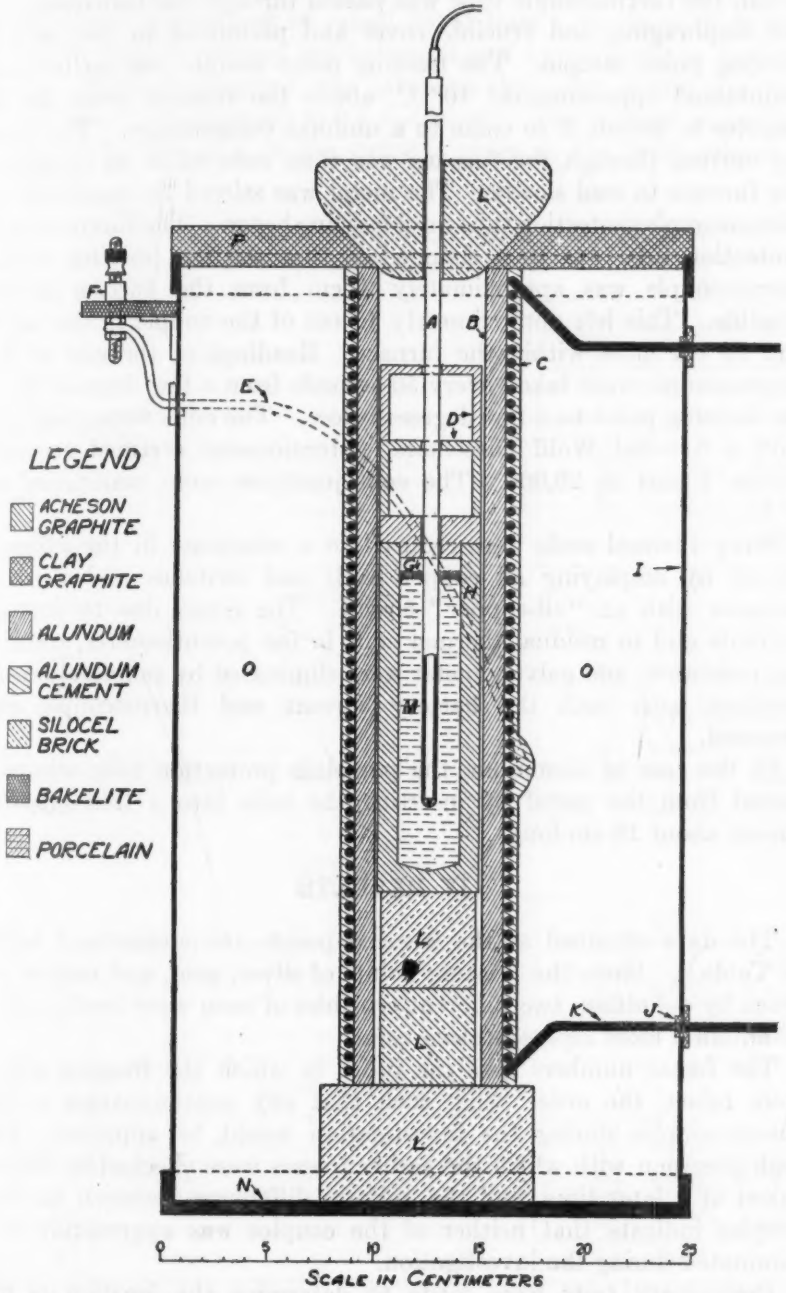

FIGURE 1.—*Furnace used in calibration of standard thermocouples at fixed points*

To determine the emf of a thermocouple at the freezing point of a metal, the thermocouple tube was passed through the furnace cover, the diaphragms, and crucible cover and permitted to rest on the freezing point sample. The freezing point sample was melted and maintained approximately 10° C. above the freezing point for 20 minutes to permit it to come to a uniform temperature. The heating current through the furnace was then reduced so as to permit the furnace to cool slowly. The metal was stirred by means of the thermocouple protection tube until freezing began. The thermocouple protection tube was then clamped so that the hot junction of the thermocouple was approximately 3 cm from the bottom of the crucible. This left approximately 10 cm of the couple in the metal and 16 cm more within the furnace. Readings of the emf of the thermocouple were taken every 30 seconds from a few degrees above the freezing point to a few degrees below. The emfs were measured with a five-dial Wolff Dieselhorst potentiometer certified accurate within 1 part in 20,000. The cold junctions were maintained at 0° C.

Stray thermal emfs were reduced to a minimum in the external circuit by employing all copper leads and switches and a galvanometer with an "all-copper" circuit. The errors due to leakage currents and to residual thermal emfs in the potentiometer, regulating resistance, and galvanometer were eliminated by taking alternate readings with both the battery current and thermocouple emf reversed.

In the case of aluminum, the porcelain protection tube was protected from the metal by inserting the tube into a thin graphite sheath about 18 cm long.

IV RESULTS

The data obtained at the freezing points are summarized below in Table 3. Since the freezing points of silver, gold, and copper are given by definition, two different crucibles of each were used in order to obtain a more representative value.

The freeze numbers give the order in which the freezing points were taken, the order being such that any contamination of the thermocouples during the investigation would be apparent. The high precision with which the earlier freezes were checked by freezes taken at a later time, and the uniform differences between the two couples indicate that neither of the couples was appreciably contaminated during the investigation.

Preliminary tests were made to determine the location of the crucible in the furnace which gave the minimum of temperature gradients within the freezing-point sample at the time freezing began. This location will give the best freezing curve for the partic-

ular cooling rate being used. The depth of immersion of the thermocouple in the freezing-point sample was such that the thermocouple could be lowered or raised by at least 1 cm from its normal position without altering the indicated emf by as much as 1 microvolt. The freezing point was taken as that part of the emf time curve which was constant to 0.3 microvolt. The number of readings obtained on this part of the curve is given in the third column of Table 3.

TABLE 3.—*Thermoelectric measurements at fixed points*

Freeze No.	Sample No.	Number of readings in freeze	International microvolts	
			E_2	E_3
COPPER POINT 1,083° C.				
1	1	34	----------	10,553.2
2	1	32	----------	10,552.4
3	1	40	10,571.6	----------
4	2	24	10,571.7	----------
5	2	24	10,571.8	----------
Mean			10,571.7	10,552.8
GOLD POINT 1,063.0° C.				
20	2	10	10,334.1	----------
21	2	10	10,334.1	----------
22	2	10	----------	10,315.9
23	2	14	----------	10,316.0
34	1	20	10,334.5	----------
35	1	18	10,334.1	----------
36	1	14	----------	10,315.8
37	1	12	----------	10,316.2
Mean			10,334.2	10,316.0
SILVER POINT 960.5° C.				
6	1	10	9,137.4	----------
7	1	16	9,137.5	----------
8	1	16	----------	9,122.2
9	1	10	----------	9,122.4
14	2	16	9,137.3	----------
19	2	20	----------	9,122.6
Mean			9,137.4	9,122.4
ALUMINUM POINT 659.23° C.				
25	1	14	5,838.9	----------
26	1	14	----------	5,831.7
30	1	18	5,839.0	----------
31	1	20	5,838.9	----------
32	1	22	----------	5,831.9
33	1	14	----------	5,831.3
Mean			5,838.9	5,831.6

TABLE 3.—*Thermoelectric measurements at fixed points.*—Con.

ANTIMONY POINT 630.52° C.

Freeze No.	Sample No.	Number of readings in freeze	International microvolts	
			E_2	E_3
10	1	32	5,541.7	
11	1	16	5,541.5	
12	1	30		5,535.0
13	1	30		5,535.0
Mean			5,541.6	5,535.0

ZINC POINT 419.47° C.

15	1	30	3,438.2	
16	1	22	3,438.1	
17	1	24		3,435.5
18	1	26		3,435.6
Mean			3,438.2	3,435.6

COPPER-SILVER EUTECTIC POINT

24	1	14	7,115.3	
27	1	24		7,105.4
28	1	24		7,105.4
29	1	20	7,115.3	
Mean			7,115.3	7,105.4

An examination of the above observations on two different crucibles of both gold and copper indicates that these points are reproducible to 0.1° C. or better. Moreover, the unpublished results of intercomparisons of thermocouples with other national laboratories indicate that the gold point is reproducible to better than 0.5° C., and probably to 0.1° C. In view of this, it seems permissible to assign values of 1,063.0° and 1,083.0° C. to the gold and copper points, respectively, since it will be shown later that the difference between these two points is 20.0° C. This is not to be understood, however, as meaning that these values are known on the Thermodynamic Centigrade Scale to this degree of accuracy.

The equations for interpolating between fixed points for both of the couples were computed for each of the four temperature scales which have been used by the Bureau of Standards since 1912. The constants of the equations are given in Tables 4 and 5. The equations are of the form $E=a+bt+ct^2$ or $E=a+bt+ct^2+dt^3$, depending upon the number of fixed points used in defining the scale. E is the emf in microvolts and t the temperature in ° C. when the cold junctions are at 0° C.

TABLE 4.—*Constants of equations for thermocouple E_2*

Temperature scale	Fixed points	Constants			
		a	*b*	*c*	*d*
Zn, Sb, and Cu	Zn, Sb, and Cu	−283.85	8.14597	0.00173372	
Zn, Al, and Cu	Zn, Al, and Cu	−280.41	8.13461	.00174128	
Zn, Sb, Ag, and Au	Zn, Sb, Ag, and Au	−319.49	8.32088	.00146639	0.00000012623
International Temperature Scale	Sb, Ag, and Au	−238.23	8.03094	.00180141	

TABLE 5.—*Constants of equation for thermocouple E_3*

Temperature scale	Fixed points	Constants			
		a	*b*	*c*	*d*
Zn, Sb, and Cu	Zn, Sb, and Cu	−281.77	8.14003	0.00172132	
Zn, Al, and Cu	Zn, Al, and Cu	−278.03	8.12764	.00172957	
Zn, Sb, Ag, and Au	Zn, Sb, Ag, and Au	−316.81	8.31197	.00145845	0.00000012420
International Temperature Scale	Sb, Ag, and Au	−236.86	8.02670	.00178808	

The calculated emfs at the fixed points and at 50° intervals from 450° to 1,100° C. are given in Tables 6 and 7.

TABLE 6.—*Temperature — emf relations for thermocouple E_2*

Temperature (° C.)	Emf in microvolts for temperature scales			
	Zn, Sb, and Cu	Zn, Al, and Cu	Zn, Sb, Ag, and Au	International Temperature Scale
419.47	[1] 3,438.2	[1] 3,438.2	[1] 3,438.2	*3,447.5*
450.00	3,732.9	3,732.8	3,733.4	*3,740.5*
500.00	4,222.6	4,222.2	4,223.3	*4,227.6*
550.00	4,720.9	4,720.4	4,721.6	*4,723.7*
600.00	5,227.9	5,227.2	5,228.2	*5,228.8*
630.52	[1] 5,541.6	5,540.9	[1] 5,541.6	[1] 5,541.6
650.00	5,743.5	5,742.8	5,743.3	5,743.0
659.23	5,839.7	[1] 5,838.9	5,839.3	5,838.9
700.00	6,267.8	6,267.0	6,267.0	6,266.1
750.00	6,800.8	6,800.0	6,799.3	6,798.3
800.00	7,342.5	7,341.7	7,340.3	7,339.4
850.00	7,892.8	7,892.1	7,890.2	7,889.6
900.00	8,451.8	8,451.2	8,449.1	8,448.8
950.00	9,019.5	9,019.0	9,017.0	9,016.9
960.50	9,139.8	9,139.3	[1] 9,137.4	[1] 9,137.4
1,000.00	9,595.8	9,595.5	9,594.0	9,594.1
1,050.00	10,180.8	10,180.7	10,180.3	10,180.3
1,063.00	10,334.4	10,334.3	[1] 10,334.2	[1] 10,334.2
1,063.00	[1] 10,571.7	[1] 10,571.7	*10,572.3*	*10,572.1*
1,100.00	*10,774.5*	*10,774.6*	*10,775.8*	*10,775.5*

[1] Calibration points.

Figures in italics represent extrapolated values.

TABLE 7.—*Temperature—emf relations for thermocouple-E_3*

Temperature (° C.)	Emf in microvolts for temperature scales			
	Zn, Sb, and Cu	Zn, Al, and Cu	Zn, Sb, Ag, and Au	International Temperature Scale
419.47	[1] 3,435.6	[1] 3,435.6	[1] 3,435.6	3,444.7
450.00	3,729.8	3,729.6	3,730.2	3,737.2
500.00	4,218.6	4,218.2	4,219.3	4,223.5
550.00	4,716.0	4,715.4	4,716.6	4,718.7
600.00	5,221.9	5,221.2	5,222.4	5,222.9
630.52	[1] 5,535.0	5,534.2	[1] 5,535.0	[1] 5,535.0
650.00	5,736.5	5,735.7	5,736.3	5,736.6
659.23	5,832.4	[1] 5,831.6	5,832.1	5,831.6
700.00	6,259.7	6,258.8	6,258.8	6,258.0
750.00	6,791.5	6,790.6	6,790.0	6,789.0
800.00	7,331.9	7,331.0	7,329.8	7,328.9
850.00	7,880.9	7,880.1	7,878.4	7,877.7
900.00	8,438.5	8,437.8	8,435.8	8,435.5
950.00	9,004.8	9,004.2	9,002.3	9,002.2
960.50	9,124.8	9,124.2	[1] 9,122.4	[1] 9,122.4
1,000.00	9,579.6	9,579.2	9,577.8	9,577.9
1,050.00	10,163.0	10,162.8	10,162.5	10,162.5
1,063.00	10,316.1	10,316.0	[1] 10,316.0	[1] 10,316.0
1,083.00	[1] 10,552.8	[1] 10,552.8	*10,553.4*	*10,553.3*
1,100.00	*10,755.1*	*10,755.2*	*10,756.4*	*10,756.1*

[1] Calibration points.
Figures in italics represent extrapolated values.

The differences between any two temperature scales as determined by thermocouple E_2 agree with the same differences obtained with E_3 to within 0.2 microvolts (0.02° C.). The average differences in degrees between any of the above scales and the International Temperature Scale (I. T. S.) are given in Table 8 for the temperature range 660° to 1,100° C.

TABLE 8.—*Differences between temperature scales*

Temperature (° C.)	I. T. S.—Zn, Sb, and Cu	I. T. S.—Zn, Al, and Cu	I. T. S.—Zn, Sb, Ag, and Au	Temperature (° C.)	I. T. S.—Zn, Sb, and Cu	I. T. S.—Zn, Al, and Cu	I. T. S.—Zn, Sb, Ag, and Au
	°C.	°C.	°C.		°C.	°C.	°C.
660	−0.08	0.00	−0.04	960.5	−0.21	−0.16	0.00
700	−.16	−.08	−.08	1,000	−.15	−.12	+.01
750	−.24	−.16	−.09				
800	−.28	−.20	−.08	1,050	−.04	−.03	.00
850	−.29	−.22	−.06	1,063	−.01	.00	.00
				1,083	+.04	+.03	−.01
900	−.26	−.21	−.03	1,100	+.08	+.08	−.03
950	−.23	−.18	−.01				

Table 8 shows (1) that the maximum difference between the International Temperature Scale and the Zn, Sb, and Cu temperature scale used by the Bureau of Standards from 1912 to 1916 is approximately 0.3° C. at 850° C.; (2) that the maximum difference between the International Temperature Scale and the Zn, Al, and Cu scale used by the Bureau of Standards from 1916 to 1926 is approximately

0.2° C. at 850° C.; and (3) that the maximum difference between the International Temperature Scale and the Zn, Sb, Ag, and Au temperature scale used by the Bureu of Standards from 1926 to 1927 is approximately 0.1° C. at 750° C.

Data previously obtained by the bureau with other couples confirms the data in column 4 of Table 8, namely, that the maximum difference between the International Temperature Scale and the Zn, Sb, Ag, and Au temperature scale is not greater than 0.1° C. These differences in column 4, Table 8, agree in magnitude but not in sign with the differences obtained by Henning and Otto.

The data of Table 8 depend upon assigning the temperatures given in Table 1,to the zinc, antimony, aluminum, silver, gold, and copper points. This naturally raises the question as to whether these same temperatures have always been assigned to the points since 1912 and whether the metals used earlier were identical with those used in this investigation. As concerns the first three points, these were determined with the resistance thermometer, calibrated at the sulphur boiling point (444.6° C. at normal atmospheric pressure), and thus a value consistent with the International Temperature Scale was always assigned to each lot of metal used. Silver, gold, and copper of very high purity have been available, and it may be taken for granted that pure metal was used in all instances. Since 1912 the temperatures assigned to these three points have been consistently those listed in Table 1.

In order to examine the reproducibility of the various temperature scales, the thermocouples were compared over the temperature range from the zinc point to 1,100° C. The hot junctions of the thermocouples were welded together in order to insure equality of temperature between these junctions of the couples. The thermocouples were then placed in a platinum wound resistance furnace and observations of the emfs of the couples taken at various temperatures. In order to eliminate errors due to slow changes in the temperature of the furnace during an observation, readings were also made of the emf between the two platinum wires and the emf between the two alloy wires. Each of these quantities is small and does not change by more than 0.1 microvolt for a temperature change of 5° C. The sum of these two emfs, therefore, gives accurately the difference between the two couples for any temperature within 5° C., of the point of observation.

The results of these observations are plotted in Figure 2. The difference between the two thermocouples as determined from the equations for any of the four temperature scales given above does not differ from the observed differences in Figure 2 by more than 0.2 microvolts (0.02° C). Thus, it is seen that with good thermocouples any of the above temperature scales are definite and reproducible to

an accuracy approaching the limit of accuracy of emf measurements. Examples of this order of reproducibility are given below.

The copper-silver eutectic point on the International Temperature Scale as determined by thermocouple E_2 is 779.39° C. The same point as determined by thermocouple E_3 is 779.41° C. The mean value of 779.4° C. is probably accurate to 0.1° C.

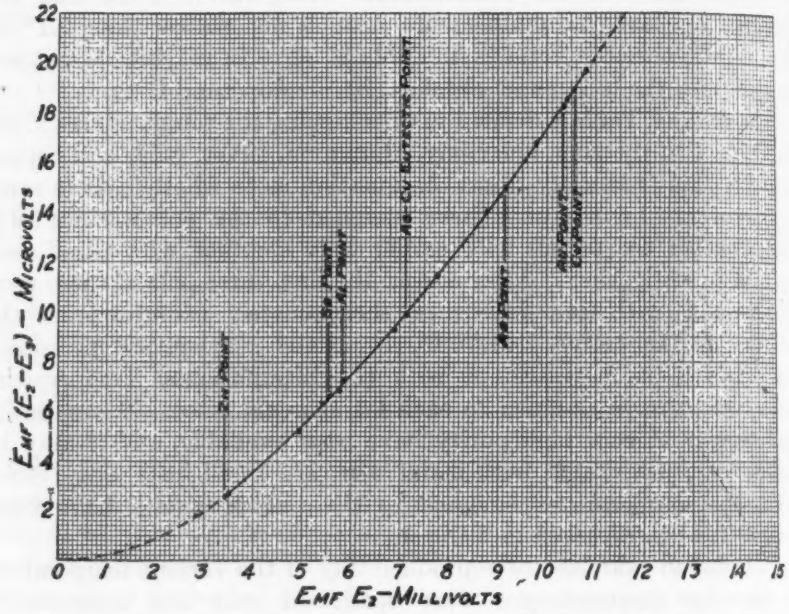

FIGURE 2.—*Observed differences in emf between thermocouples E_2 and E_3*

The difference between the freezing points of gold and copper as determined by each of the above temperature scales is given in Table 9.

TABLE 9.—*Difference between freezing points of gold and copper*

Temperature scale	Difference in °C. by thermocouple	
	E_3	E_2
International Temperature Scale	19.97	19.96
Zn, Sb, Ag, and Au scale	19.95	19.93
Zn, Al, and Cu scale	20.01	20.00
Zn, Sb, and Cu scale	20.02	20.01
Mean	19.98	

The values on the first two scales in the table are obtained by extrapolating above the gold point to obtain the copper point whereas the values by the last two scales in the table are obtained by

interpolating to obtain the gold point. Therefore, if a value of 1,063.0° C. is assigned to the freezing point of gold, a value of 1,083.0° C. should be assigned to the freezing point of copper.

V. SUMMARY AND CONCLUSIONS

The differences between four widely used thermoelectric temperature scales based upon (1) Sb, Ag, and Au; (2) Zn, Sb, Ag, and Au; (3) Zn, Al, and Cu; and (4) Zn, Sb, and Cu, as calibration points with the temperatures given in Table 1, have been determined. The maximum difference between (1) and (2) was found to be 0.1° C., between (1) and (3) 0.2° C., and between (1) and (4) 0.3° C.

A comparison of the differences between the calibration curves for two thermocouples with the differences between the two couples found by direct measurement indicates that any of the above temperature scales are reproducible to better than 0.1° C.

The freezing point of the copper-silver eutectic alloy 71.9 per cent silver and 28.1 per cent copper, on the International Temperature Scale was found to be 779.4° C. ± 0.1° C.

The difference between the freezing points of gold and copper was found to be 20.0° C. ± 0.1° C.

Methods used at the Bureau of Standards in realizing the International Temperature Scale in the range 660° to 1,063° C. are described in detail.

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WASHINGTON, April 23, 1929.

LIGHT FASTNESS OF LITHOGRAPHIC INK PIGMENTS

By William D. Appel and Robert F. Reed

ABSTRACT

One hundred and thirty-six specially prepared lithographic prints, representing 31 pigments, were exposed to daylight in several different ways and to the light from a glass-inclosed carbon arc. The fading observed is reported in this paper, and a classification of the fastness of the pigments as used in lithographic inks is given.

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I. INTRODUCTION

A study of the light fastness of lithographic ink pigments was made through the cooperation of the Lithographic Technical Foundation (Inc.) and the Bureau of Standards. The foundation selected the pigments, prepared the inks, and from them the printed samples which were exposed at the Bureau of Standards to daylight under various conditions and to the light from a glass-inclosed carbon arc. The results of these experiments are recorded in this paper.[1]

One of the objects of the exposures was to determine whether the prints in a series show the same relative fading when they are exposed under different daylight conditions. Another object was to investigate the suitability of the carbon arc lamp for laboratory tests. A third object was to find suitable standards of fastness to light. Since all of the inks were exposed simultaneously in each type of test, a classification of their relative fastness is possible.

[1] This work was carried out simultaneously with an elaborate series of tests of dyed fabrics conducted by the American Association of Textile Chemists and Colorists and the Bureau of Standards during the summers of 1926 and 1927. A report on the dyed fabrics will be found in the American Dyestuff Reporter for June 24, 1929. Although the tests were planned from the standpoint of dyed fabrics, they were found applicable to lithographic prints, and the results obtained with the prints are of sufficient interest to be placed on record.

II. PROCEDURE

1. PREPARATION OF SAMPLES

To provide material for the tests, 31 of the pigments and lake colors more commonly used in lithographic and "offset" inks were selected. These were ground in "burnt" lithographic varnish with the necessary additions of bases and driers to produce inks having good working qualities. The bases consisted of aluminum hydrate, mixtures of aluminum hydrate with blanc fixe, commonly known as "gloss white," and magnesium carbonate. The driers consisted of lead and manganese resinates and linoleates. A total of 34 inks were prepared which in every respect were comparable with commercial "offset" inks. Detailed information regarding the compositions of the inks is given in Table 1.

Solid impressions of these inks were made by means of an offset proving press on a good grade of white, machine-finished paper, care being taken to secure medium prints, not undercharged or overcharged with ink. Each ink was printed in four strengths, as follows:

1. 1 part ink, 25 parts laketine.
2. 1 part ink, 10 parts laketine.
3. 1 part ink, 5 parts laketine.
4. Full-strength ink.

Laketine is a white ink used for diluting colored inks to produce tints. The laketine used in this work consisted of 4 parts of magnesium carbonate, 2 parts of aluminum hydrate, and 1 part of lead carbonate in a vehicle composed of lithovarnish, with some rosin and water. In all, 136 prints were used in the tests.

TABLE 1.—*Samples used and results obtained in the light exposures*

TABLE 1.—*Samples used and results obtained in the light exposures*

Serial No.[1]	Colour Index No.	Name of pigment	Approximate concentration in percentage of coloring matter in pigment	Additional base parts added per 100 parts of pigment	Ratio coloring matter to total base	Approximate total solids in ink	Approximate coloring matter in ink	Dilution of ink with laketine	Other constituents	Fastness class	Special characteristics
						Per cent	*Per cent*				
1101	1270	Chrome yellow, C. P. lemon	100	15 (gloss white)	67-10	70	61	1-25	Drier	5	Becomes progressively duller but does not fade appreciably.
2								1-10	do	5	
3								1- 5	do	5	
4								1- 0	None	5	
1105	1270	Chrome yellow, C. P. medium	100	do	67-10	70	61	1-25	Drier	5	Do.
6								1-10	do	5	
7								1- 5	do	5	
8								1- 0	None	5	
1109	640	Tartrazine, barium lake	[2] 40	0	2- 3	55	22	1-25	Drier	2	Fades less in north skylight than in sun exposure,[3] slight dulling precedes fading.
10								1-10		2	
11								1- 5		2	
12								1- 0		3	
1113	10 and 655.	Naphthol yellow S and auramine, barium lake.	[2] 20	0	1- 4	55	11	1-25	do	1	Fades slightly less in north skylight and slightly more in arc light than in sun exposure; [3] dulling precedes regular fading.
4								1-10		1	
5								1- 5		1	
6								1- 0		2	
1117	1270	Chrome orange, C. P. dark	100	66.7 (gloss white)	3- 2	72	43	1-25	do	5	Becomes slightly duller on exposure but does not fade appreciably.
8								1-10	do	5	
9								1- 5	do	5	
20								1- 0	None	5	
1121	151	Acid orange II, tin lake	[2] 30	0	10-23	50	15	1-25	Drier	1	Fades slightly less in north skylight than in sun exposure; [3] very fugitive.
2								1-10		1	
3								1- 5		1	
4								1- 0		1	

[1] Samples whose serial numbers are followed by "x," like 1133x, were exposed simultaneously with set K samples and not with set A.
[2] On aluminum hydrate.
[3] When the exposures are timed to produce the same average fading in the group of samples in the 2 types of exposure.

TABLE 1.—*Samples used and results obtained in the light exposures*—Continued

Serial No.	Colour Index No.	Name of pigment	Approximate concentration in percentage of coloring matter in pigment	Additional base parts added per 100 parts of pigment	Ratio coloring matter to total base	Approximate total solids in ink	Approximate coloring matter in ink	Dilution of ink with laketine	Other constituents	Fastness class	Special characteristics
						Per cent	*Per cent*				
1125								1–25		1	
6	151	Acid orange II, barium lake	[4] 40	0	2– 3	50	20	1–10	Drier	1	Fades slightly less in north skylight than in sun exposure; [3] very fugitive.
7								1– 5		1	
8								1– 0		1	
1129								1–25		1	
30	165	Lake red C, sodium toner	100	100 (gloss white)	1– 1	50	25	1–10	do	1	Fades less in north skylight and in the arc light than in sun exposure; [3] slight dulling precedes fading.
1								1– 5		2	
2								1– 0		3	
1133x								1–25		1	
4x		Permanent red R [5]	100	do	1– 1	50	25	1–10	do	3	Fades slightly more in the arc light than in sun exposure; [3] slight dulling precedes fading.
5x								1– 5		4	
6x								1– 0		5	
1137								1–25	do	4	
8	1280	English vermilion (mercury sulphide).	100	5 (gloss white)	20– 1	80	76	1–10	do	4	Becomes progressively duller but does not fade appreciably.
9								1– 5	do	4	
40								1– 0	None	5	
1141x								1–25		1	
2x	165	Lake red C, barium toner	100	100 (gloss white)	1– 1	60	32	1–10	Drier	1	Fades slightly less in the arc light than in sun exposure. [3]
3x								1– 5		2	
4x								1– 0		4	
1145x								1–25		2	
6x	69	Toluidine red toner	100	do	1– 1	50	25	1–10	do	3	Fades slightly less in north skylight and slightly more in the arc light than in sun exposure; [3] slight dulling precedes fading.
7x								1– 5		4	
8x								1– 0		5	
1149x								1–25		1	
50x	189	Lithol red R, sodium toner	100	do	1– 1	50	25	1–10	do	1	Fades slightly more in the arc light than in sun exposure; [3] becomes dull and loses bronze before fading.
51x								1– 5		2	
52x								1– 0		4	
1153x								1–25		1	
4x	189	Lithol red R, barium toner	100	do	1– 1	50	25	1–10	do	1	Becomes distinctly bluer and duller before fading appreciably; loses its bronze quickly.
5x								1– 5		2	
6x								1– 0		4	

1153x 4x 5x 6x	189	Lithol red R, barium toner	100	do	1- 1	50	25	1-25 1-10 1- 5 1- 0	do	1 1 2 4	Becomes distinctly bluer and duller before fading appreciably; loses its bronze quickly.
1157x 8x 9x 60x	189	Lithol red R, calcium toner	100	do	1- 1	50	25	1-25 1-10 1- 5 1- 0	do	1 1 2 4	Loses its bronze and becomes duller before fading.
1161 2 3 4	189	Lithol red R, sodium toner	100	100 (magnesium carbonate).	1- 1	50	25	1-25 1-10 1- 5 1- 0	do	1 1 2 4	Fades slightly more in the arc light than in sun exposure;[3] becomes dull and loses bronze before fading.
1165 6 7 8	189	Lithol red R, barium toner	100	do	1- 1	50	25	1-25 1-10 1- 5 1- 0	do	1 1 2 4	Becomes bluer and duller before fading appreciably.
169 70 71 72	189	Lithol red R, calcium toner	100	do	1- 1	50	25	1-25 1-10 1- 5 1- 0	do	1 1 2 4	Do.
1173 4 5 6	216	Pigment scarlet 3B, barium lake.	[4] 34	0	10-19	60	20	1-25 1-10 1- 5 1- 0	do do do None	1 2 5 5	Fades less in arc light than in sun exposure;[3] becomes much bluer and duller before fading appreciably.
1177 8 9 80	163	Lithol rubine B, calcium lake	50	50 (gloss white)	1- 2	60	20	1-25 1-10 1- 5 1- 0	Drier	2 3 4 5	Becomes slightly bluer and dull before fading appreciably.
1181 2 3 4	1027	Madder lake	[5] 25	0	1- 3	36	9	1-25 1-10 1- 5 1- 0	do do do None	4 4 5 5	Fades slightly less in the arc light than in sun exposure;[3] becomes dull before fading appreciably.
1185 6 7 8 [illegible]	44	Para toner, light	100	100 (gloss white)	1- 1	50	25	1-25 1-10 1- 5 1- 0	Drier	1 2 3 5	Fades slightly more in the arc light than in sun exposure;[3] becomes slightly dull before fading.
1189 90 91 92	44	Para toner, dark	100	do	1- 1	50	25	1-25 1-10 1- 5 1- 0	do	1 1 2 5	Fades slightly less in north skylight and slightly more in the arc light than in sun exposure;[3] becomes slightly dull before fading.

[3] When the exposures are timed to produce the same average fading in the group of samples in the 2 types of exposure.
[4] On gloss white.
[5] 2-chloro-4-nitrobenzene-azo-2-naphthol.
[6] Base not known.

TABLE 1.—*Samples used and results obtained in the light exposures*—Continued

Serial No.	Colour Index No.	Name of pigment	Approximate concentration in percentage of coloring matter in pigment	Additional base parts added per 100 parts of pigment	Ratio coloring matter to total base	Approximate total solids in ink	Approximate coloring matter in ink	Dilution of ink with laketine	Other constituents	Fastness class	Special characteristics
						Per cent	*Per cent*				
1193	680	Methyl violet, tannin toner	100	100 (gloss white)	1–1	50	25	1–25	Drier	1	Blackens and loses its bronze before fading; very fugitive.
4								1–10		1	
5								1– 5		1	
6								1– 0		2	
1197	680	Methyl violet, tungstic toner	100	do	1–1	50	25	1–25	do	1	Becomes dull before fading; fades considerably slower than tannin lake.
8								1–10		1	
9								1– 5		1	
1200								1– 0		3	
1201	1288	Milori blue, C. P. light (soda)	100	0	No base.	50	50	1–25	do	5	Becomes dull but does not fade; exposure increases bronze of full strength print.
2								1–10	do	5	
3								1– 5	do	5	
4								1– 0	None	5	
1205	1288	Milori blue, C. P. medium (soda)	100	0	No base.	50	50	1–25	Drier	5	Do.
6								1–10	do	5	
7								1– 5	do	5	
8								1– 0	None	5	
1209	1288	Bronze blue, C. P. (potash)	100	0	No base.	55	55	1–25	Drier	5	Do.
10								1–10	do	5	
11								1– 5	do	5	
12								1– 0	None	5	
1213	704	Alkali blue, green shade	100	0	1– 0	50	50	1–25	Drier	2	Fades slightly less in the arc light than in sun exposure;[1] becomes dull and loses bronze gradually.
4								1–10		2	
5								1– 5		3	
6								1– 0		4	
1217	704	Alkali blue, red shade	100	0	No base.	50	50	1–25	do	2	Fades slightly less in the arc light than in sun exposure;[1] becomes dull and loses bronze.
8								1–10		2	
9								1– 5		3	
20								1– 0		4	

1221	1290	Ultramarine blue	100	16.7 (gloss white)	6– 1	65	56	1–25	do	2	Becomes duller and redder before fading appreciably.
2								1–10	do	3	
3								1– 5	do	5	
4								1– 0	None	5	
1225	671	Peacock blue (erioglaucine, barium lake).	[2] 35	0	10–19	50	17.5	1–25	Drier	1	Very fugitive; blackens first and then fades.
6								1–10		1	
7								1– 5		1	
8								1– 0		1	
1229	1308	Carbon black	100	0	No base.	33	33	1–25	do	5	Practically no change on exposure.
30								1–10		5	
1								1– 5		5	
2								1– 0		5	
1233	1298	Chrome green [1]	100	25 (gloss white)	4– 1	75	60	1–25	do	5	Becomes progressively duller but does not fade.
4								1–10	do	5	
5								1– 5	do	5	
6								1– 0	None	5	
1237		Sample of white M. F. paper on which prints were made.									Becomes distinctly brown in sun exposures up to 96 hours, after which it bleaches perceptibly but does not completely return to its original whiteness.

[2] On aluminum hydrate.
[1] When the exposures are timed to produce the same average fading in the group of samples in the 2 types of exposure.
[1] 3 parts primrose yellow, 1 part milori blue C. P. light.

2. METHOD OF EXPOSURE

(a) SUN AND DAYLIGHT EXPOSURES

The prints were cut into pieces which were mounted on heavy opaque black paper and labeled as shown in Figure 1. Six complete sets of samples were thus prepared. Each set was designated by a letter and each sample in the set by the serial number of the print from which it was cut.

The individual samples of each set were assembled in numerical order, 25 in a row, beginning on the right, and attached to one another with wire staples along the bottom, so that each sample overlapped the left-hand half of the preceding sample. In this manner the opaque backing of sample A 1102 masked the left-hand half of sample A 1101, etc. The cardboard chips on the upper and lower right-hand corners of each sample (fig. 1) served as guides for the covering sample, so that it could be removed at any time in order to examine the sample under it and replaced exactly in its original position. The samples thus mounted were fastened on boards as shown in Figure 2.

The exposure racks are located on the roof of the Industrial Building, Bureau of Standards, Washington, D. C. They are shown in Figures 3 and 4. The racks run east and west and are open to the full light of the sky. The samples, mounted on boards, were exposed to light by placing them in the racks as shown.

The glass covers were set at a distance of ½ inch from the samples, and provision was made for free access of air to the latter. The covers were 5 inches larger in each direction than the boards supporting the samples, so that there was no significant shading by the framework of the cover. Ordinary window glass was used. It was purchased under a specification which required selection for uniformity in color, thickness, and composition. By actual measurement the minimum and maximum thicknesses of the pieces used were 0.112 and 0.139 inch, respectively, and the average thickness was 0.125 inch. The spectral transmission of two samples of the glass taken at random is shown in Figure 5. The glass covers were cleaned frequently.

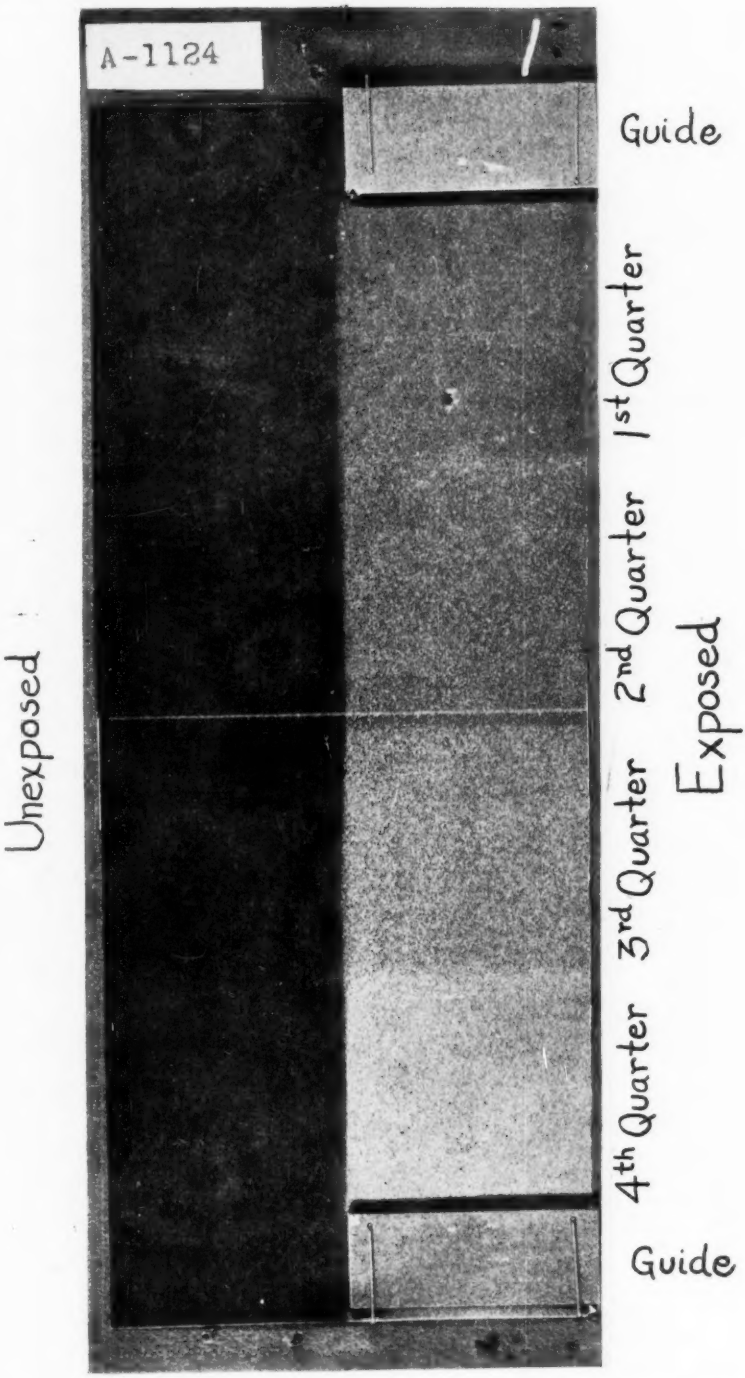

FIGURE 1.—*Sample (after exposure) showing method of mounting, and the four exposed areas*

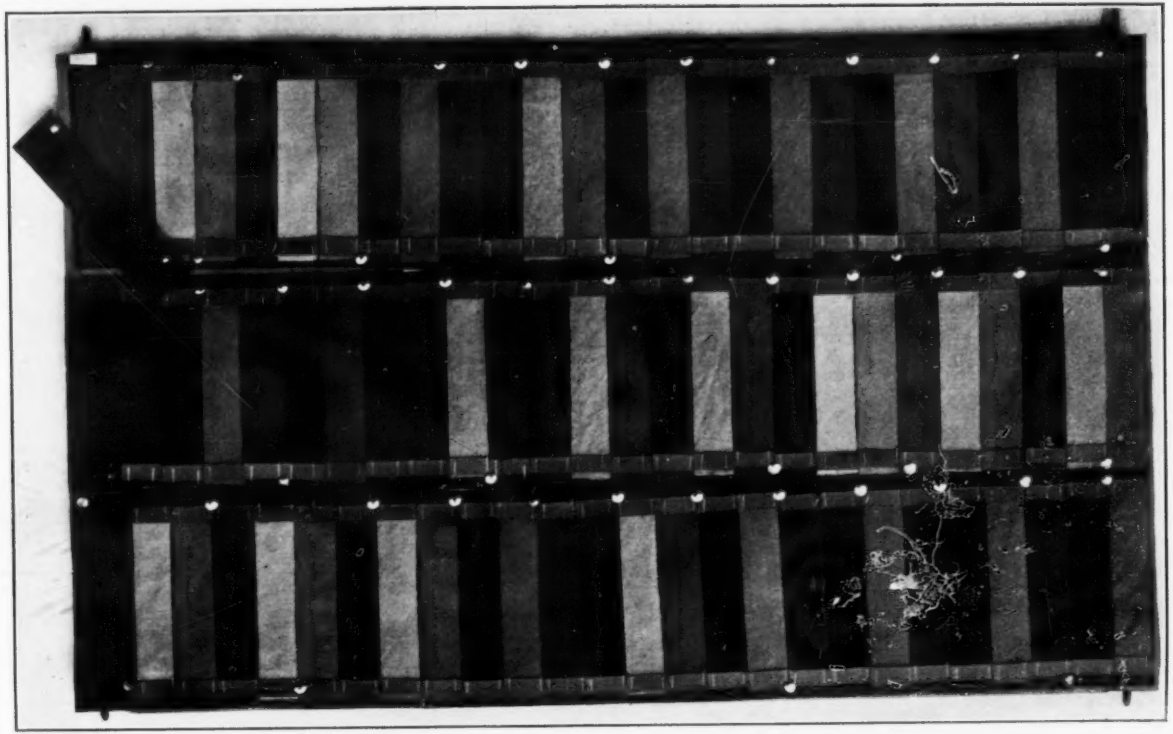

FIGURE 2.—*Samples mounted on board ready for exposure*

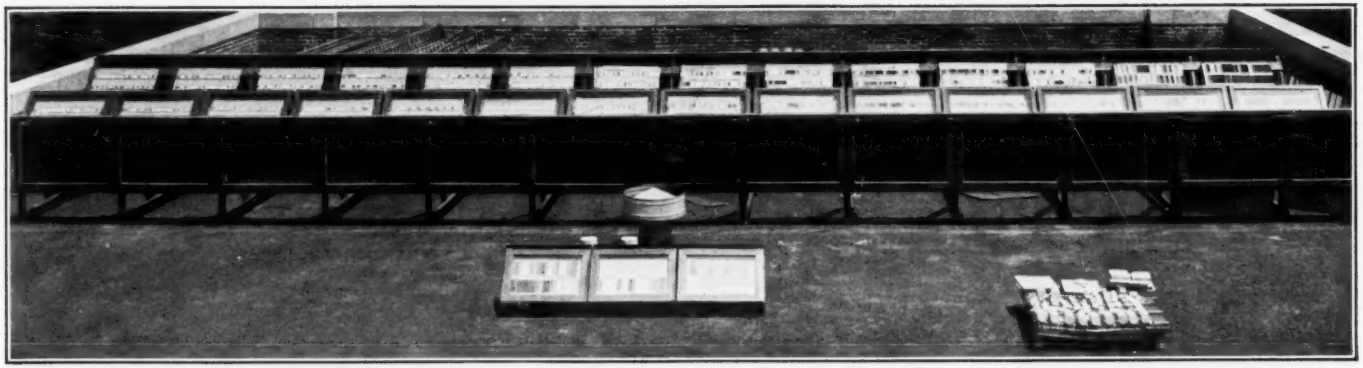

FIGURE 3.—*Exposure rack (from the south)*

FIGURE 4.—*One of the exposure racks (near view)*

The six duplicate sets of samples were exposed during the summer and autumn months under the following conditions:

Set A. Exposed only on clear days between 9 a. m. and 3 p. m. under glass, at an angle of 45° from the horizontal facing south. If clouds came up, the samples were promptly covered.

Set B. Simultaneously with set A and under the same conditions except that no glass cover was used over the samples.

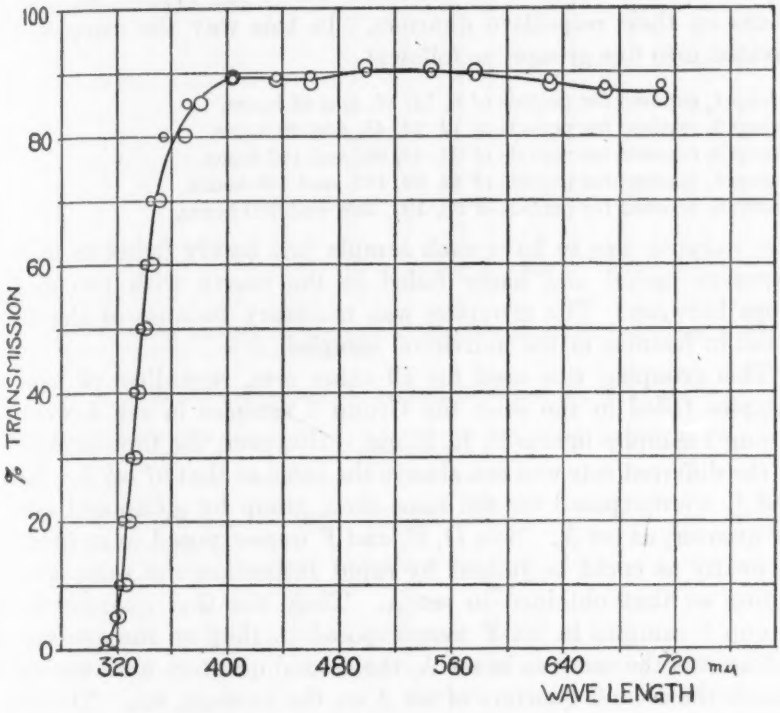

FIGURE 5.—*Spectral transmission of cover glass*

Set D. Exposed continuously day and night, regardless of the weather, under glass, vertical, facing south.

Set E. Exposed continuously, under glass, at an angle of 45° facing south.

Set F. Exposed continuously, under glass, vertical, facing north.

Set K. Exactly like set A but during the summer of 1927, the set A exposures having been made principally in 1926.

Set A was taken as the standard in timing the exposures. When placed in the rack and exposed for 6 hours, such set A samples as showed an alteration in color were remounted separately and labeled Group 1. Then the upper fourth of the exposed portions of these prints was covered with black opaque cardboard, and the remaining

three-fourths was exposed for 6 hours longer. The cardboard was then moved so as to cover the second quarter in addition to the first. This was continued until the four quarters of the Group 1 prints had received 6, 12, 24, and 48 hours exposure, respectively.

The prints of set A which did not show an alteration in color in the first 6 hours were exposed for 6 hours longer on the first quarter, after which those samples showing an alteration were remounted separately and exposed as described above for 12, 24, 48, and 96 hours on their respective quarters. In this way the samples were divided into five groups, as follows:

Group 1, exposed for periods of 6, 12, 24, and 48 hours.
Group 2, exposed for periods of 12, 24, 48, and 96 hours.
Group 3, exposed for periods of 24, 48, 96, and 192 hours.
Group 4, exposed for periods of 48, 96, 192, and 384 hours.
Group 5, exposed for periods of 96, 192, 288, and 480 hours.

The purpose was to have each sample just barely faded in the first exposure period and badly faded in the fourth with two distinct steps between. The grouping was necessary because of the differences in fastness of the individual samples.

This grouping was used for all other sets, regardless of how the samples faded in the sets; the Group 1 samples in set A were the Group 1 samples in sets B, K, F, etc. However, the time of exposure of the different sets was not always the same as that of set A. Sets B and K were exposed for the same time, group by group and quarter by quarter, as set A. Sets D, E, and F were exposed so as to obtain as nearly as could be judged by rapid inspection the same average fading as that obtained in set A. Thus, the first quarters of the Group 1 samples in set F were exposed so that on the average the fading was the same as in set A, the second quarters were exposed to match the second quarters of set A on the average, etc. The object of this procedure was to determine the time required to produce the same amount of fading in the different exposures and the effect of the different conditions of exposure on the relative fading of individual colors.

A summary of the time of exposure of the different sets is given in Table 2. The average temperature and relative humidity of the air during the exposures are given in Table 3.

TABLE 2.—*Time of exposure of the samples*

Group	Quarter	Sets A, B, and K	Set D	Set E	Set F	Sets G-H
		Hours	*Days*	*Days*	*Days*	*Hours*
1	1	6	2.3	0.7	3	2.3
	2	12	4	2.2	4.7	4.7
	3	24	6.3	4	11	9.3
	4	48	14	6.6	17	18.7
2	1	12	4	2.2	4.7	4.7
	2	24	6.3	4	11	9.3
	3	48	14	6.6	22	18.7
	4	96	32	12.7	61	37.3
3	1	24	9	[1] 9	34	9.3
	2	48	17.3	[1] 17	70	18.7
	3	96	31	17	149	37.3
	4	192	49	31	260	74.7
4	1	48	19	10.5	6	18.7
	2	96	31.3	20	9.5	37.3
	3	179.3	49	41.3	27.1	74.7
	4	275.7	84	65.3	83.8	149.3
5	1	96	35	26	[2] 30	37.3
	2	192	64	53	[2] 70	74.7
	3	288	101	106	[2] 146	149.3
	4	480	144	167	[2] 260	298.7

[1] Overexposed.
[2] These exposures were not carried to completion because of the time required and because most of these samples did not fade even in the set A exposure.

TABLE 3.—*Temperature and relative humidity of the air*

[The average of observations made at 9 a. m., 12 noon, and 3 p. m. on days when samples were exposed are given]

Set	Temperature	Relative humidity
A	44	25
K	39	26
B	32	46
D	33	43
E	42	35
F	25	45

TABLE 4.—*Spectral distribution of the radiation* [1] *from the glass-inclosed arc lamp compared with sunlight at Washington, D. C., on May 25, 1926, 11 a. m. to 12 noon*

Spectral range (in mμ)	Percentage of the total radiation	
	Arc	Sun
170 to 320	0.0	2.0
320 to 360	2.0	2.8
360 to 480	18.5	12.6
480 to 600	9.3	21.9
600 to 1,400	16.5	38.9
1,400 to 4,200	22.1	21.4
4,200 to 12,000	31.6	0.4

[1] Measurements by W. W. Coblentz, Bureau of Standards.

After the exposures made during 1926 were completed it was found that the prints of a number of the colors were too lightly inked. Fresh prints of these were made and were exposed during 1927. These samples were designated with an x after the sample number (see 1133x in Table 1).

(b) CARBON ARC LIGHT EXPOSURES

The commercially available inclosed carbon arc lamp known as the "fade-ometer" was used for these tests because it runs without attention for over 24 hours, and because it is in rather general use in industrial laboratories for this purpose. It is a glass-inclosed arc, giving little or no radiation below a wave length of 320 mμ, but much from 350 to 480 mμ. Its spectral distribution in comparison with sunlight is given in Table 4. The solid carbons furnished with the lamp were used. The "fade-ometer" was operated on a 230 to 240 volt d. c. circuit at 12 to 13 amperes. The samples were placed in the holders provided with the apparatus and were thus exposed at a distance of 10 inches from the axis of the arc. Two of the lamps were used in making the tests.

The arc exposures were made on set G-H, which was identical with those previously described, except that the samples were cut to measure 2¼ by 3 inches, so that they would go in the "fade-ometer" holders. For this reason only two different exposures could be made on each sample and two samples were required. G samples were given exposures corresponding to the first and second quarters of set A sun exposures, and H samples were given exposures corresponding to the third and fourth quarters of set A. A piece of thin sheet aluminum was used to shield one half while exposure of the other half was being completed.

According to the manufacturer, one "fade-ometer" hour is equivalent to 1.3 hours of summer sunlight for textiles and 5 hours of summer sunlight for printing inks. The lithographic prints, however, did not fade as much in 1.2 "fade-ometer" hours as in 6 hours exposure to sunlight at Washington, and it was determined by close observation of the prints that 2.33 "fade-ometer" hours was approximately equivalent to 6 hours' sun exposure for the inks. Longer exposures gave the same time ratio for equivalent fading.

In making the arc exposures, interruptions were avoided as far as possible. Each sample was exposed for approximately half the time in the upper row of openings and the other half in the lower row, since it is claimed that somewhat more fading is produced in the upper row than in the lower in a given length of time.[2] The receptacles below the lamps were supplied with water at all times, and the globes

[2] Gordon, Am. Dyestuff Reporter, **14**, p. 488; 1925.

were cleaned daily. No difficulties were experienced in the operation of the machines.

The maximum temperature indicated by a mercury thermometer, the bulb of which was covered with black paper and placed near the samples during exposure to the arc, was 80° C. Without the covering of black paper the maximum observed temperature was 70° C.

3. METHOD OF STUDYING RESULTS

As stated above, set A was exposed so as to produce as far as practicable a barely noticeable fading of the first quarter of each sample. By this means set A was subdivided into five groups according to the time necessary to produce this result. After the group exposures were completed the fading of all four quarters of each sample was carefully studied, checked against set K exposures, and the samples finally classified in the following way which, in many instances, led to results differing from the tentative grouping used in making the exposures.

Class 1. All samples showing marked alteration or fading at the end of 6 hours' exposure.

Class 2. Samples showing but slight alteration in 6 hours, distinct alteration in 12 hours, and more and more alteration in 24 and 48 hours' exposure.

Class 3. Samples showing but slight alteration in 12 hours, distinct alteration in 24 hours.

Class 4. Samples showing but slight alteration in 24 hours and distinct alteration 48 hours.

Class 5. Samples showing but slight alteration in 48 hours' exposure.

Very much longer exposures would be needed to split off a still faster class from class 5.

The difference in fastness between these classes is sufficient to make possible a clear-cut classification of most of the samples. Naturally there are some which exhibit intermediate degrees of fastness. Others do not fade in regular steps, so that their satisfactory classification is difficult. The behavior of all four quarters was considered in judging the fastness of such samples.

Certain effects other than simple fading of the pigment were observed and were also carefully considered in determining the classification. These effects were:

1. The paper darkened during the shorter exposures sufficiently to cause pale colors to appear dull. This darkening of the paper became less marked after longer exposure because of the bleaching action of light.
2. Samples originally having a bronzy appearance usually lost it more or less completely in six hours' exposure to sunlight.
3. The yellowing of the varnish vehicle in the absence of light and its bleaching in strong light caused the unexposed portions of certain blue samples to appear greener than the exposed portions.

4. Certain samples developed a somewhat different color at the increased temperature of the exposure and could properly be judged only after allowing them to cool. Several days elapsed before some of the samples returned to their original color in the unexposed portion.

The other exposures (sets B, D, E, F, and G-H) were compared individually with the corresponding samples in sets A and K to determine which prints faded more or less than the average under the various conditions. The more important deviations are pointed out in Table 1 under "special characteristics." Table 5 gives the number of samples in each set which faded "more" than, "slightly more" than, "equal" to, "slightly less" than, and "less" than the corresponding samples in set A in this comparison.

TABLE 5.—*Summary of comparisons with set A*

[The columns give the number of samples that are "less," "slightly less," "equal," "slightly more," or "more," faded than the corresponding samples in set A]

Group	Set B					Set D					Set E					Set F					Set G–H					Set K				
	Less	Slightly less	Equal	Slightly more	More	Less	Slightly less	Equal	Slightly more	More	Less	Slightly less	Equal	Slightly more	More	Less	Slightly less	Equal	Slightly more	More	Less	Slightly less	Equal	Slightly more	More	Less	Slightly less	Equal	Slightly more	More
1	0	20	63	5	0	9	15	57	5	2	0	0	64	19	5	14	14	47	7	6	7	6	61	2	12	0	0	56	5	13
2	0	2	28	2	0	3	2	24	3	0	0	0	27	5	0	4	0	23	3	2	5	3	21	0	3	0	0	18	7	1
3	0	0	13	8	3	0	1	21	2	0	0	2	20	1	1	1	1	14	7	1	2	3	17	2	0	0	0	22	0	0
4	0	0	2	0	0	0	0	2	0	0	0	0	0	2	0	0	0	2	0	0	0	0	2	0	0	0	0	0	0	0
5	0	0	12	2	0	0	0	14	0	0	0	0	12	2	0	0	0	14	0	0	0	0	8	1	5	0	0	14	0	0
Total	0	22	118	17	3	12	18	118	10	2	0	2	123	29	6	19	15	100	17	9	14	12	109	5	20	0	0	110	12	14

III. RESULTS

The classification of the prints according to fastness is shown in Table 1. In using these results it must be remembered that the resistance of a film of ink to the action of light is affected by its thickness and transparency, factors which are difficult to control. This, together with the variability of pigments made from nominally the same materials by different manufacturers, would make it difficult to reproduce exactly the results which were obtained from this particular set of prints. However, the results given here should be a useful guide in the classification of similar pigments from other sources.

The comparison of the samples in set K with those in set A, given in Table 5, shows that exposure under the conditions represented by these two sets can be duplicated reasonably well, though some samples in set K are more faded than their duplicates in set A. This type of exposure has been adopted by the American Association of Textile Chemists and Colorists as a standard sunlight exposure. It

can be recommended for lithographic prints where a drastic sunlight exposure test is desired.

The fading of set B is very similar to that of sets A and K. The presence or absence of the glass cover evidently affects the fading of relatively few samples.

Sets D, E, and F, which were exposed continuously, can not be duplicated because of varying weather conditions. It was observed (see Table 5 and also Table 1, "special characteristics") that certain samples faded more and others less in set F than in set A. This behavior was noticed to a less extent in sets D and E. It was not as pronounced in the printing ink tests as in similar tests of dyed textiles. (See footnote 1, p. 359.) These differences in relative fading among samples in one set compared with those in another are to be attributed in part, at least, to the different light intensities and environmental conditions during the exposures. Sets A and K were exposed to light of high intensity and set F in particular to light of low intensity. The temperature of the set F exposures was, on the average, nearly 20° C. lower than that of set A exposures. (See Table 3.) The relative humidity of the atmosphere at the samples was 20 per cent higher for set F than for set A.

From the data given in Tables 2 and 5 it is obvious that the time required to produce the same amount of fading in the several types of daylight exposures is different with different samples and on different days. In a very general way 6 hours' exposure under the conditions of set A is equivalent to 1 day under the conditions of set E, 2 days of set D, and 3 days of set F. (See reference in footnote 1 for the wide variability in this respect of individual samples of dyed textiles.)

Set G–H, the arc lamp exposure, should be duplicable. The majority of the arc exposures match the sunlight exposures, set A, rather closely. Two and one-third hours' exposure in the "fadeometer" is practically equivalent to six hours' exposure to sunlight between 9 a. m. and 3 p. m. at Washington, D. C. during summer and autumn. Samples showing markedly exceptional behavior in the arc exposure are indicated in Table 2 under "special characteristics." (See also Table 5.)

With due regard to the exceptional samples, the results of these tests indicate that certain prints may be selected for use as standards of fastness to light. Some additional work will be necessary, however, to develop a simple, practical means of preparing the standards and making the tests.

64338°—29——3

IV. ACKNOWLEDGMENTS

The cooperation of the following firms in furnishing and preparing material and in giving information and advice in connection with these tests is gratefully acknowledged: Acme Printing Ink Co., American Aniline Products Co., California Ink Co., Charles Eneu Johnson & Co., Latham Litho. & Printing Co., Max Marx Color & Chemical Co., and Philip Ruxton (Inc.). The Atlas Electric Devices Co., of Chicago, very kindly placed two new "fade-ometers" at our disposal for these tests.

V. SUMMARY

1. Although the relative fading of a majority of the lithographic prints is the same in the different exposures, a few fade decidedly faster and others slower than the average in certain exposures.

2. The yellowing of the varnish in the absence of light and its bleaching in strong light must be taken into consideration in judging the fastness of pale colors.

3. The heat during exposure affects certain prints and causes a reversible change in color.

4. The carbon arc lamp appears to be a reasonably satisfactory source of light for fading tests of lithographic inks. It is possible that better agreement with sun exposures would be obtained if the samples were placed far enough from the arc to fade at about the same rate as in sunlight, and if the temperature were controlled so that the samples would not be heated above the temperature reached in the exposures to sunlight (approximately 44° C.).

5. A classification of the fastness of 136 samples representing 31 pigments is given. Since the fastness of a given pigment depends on its concentration in the ink film of the print, each pigment may be given more than one fastness classification, according to its concentration.

WASHINGTON, April 12, 1929.

EFFECT OF OXIDIZING CONDITIONS ON ACCELERATED ELECTROLYTIC CORROSION TESTS

By Henry S. Rawdon and W. A. Tucker

ABSTRACT

Accelerated electrolytic corrosion tests were made on sheet copper and nickel in a sodium-chloride solution. Both anode and cathode were of the same metal, and the applied emf was relatively very low; the results are expressed as loss-of-weight-potential curves. The effect of oxidizing conditions was studied by surrounding the cell by an atmosphere of oxygen or nitrogen and/or dissolving the same gas in the electrolyte. The results clearly show the accelerating effect of oxygen on corrosion by reducing the potential necessary for a given corrosion rate. The results also have a distinct bearing on the theory of underwater corrosion as affected by conditions of differential oxidation within the solution.

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I. INTRODUCTION

An electrolytic method based on the assumption that corrosion is essentially electrolytic in its nature—that is, it involves two distinct processes, anodic and cathodic—was recently described[1] as a logical procedure for studying corrosion phenomena. In this report the principles were outlined which, it was felt, must be observed if results consistent with "natural" corrosion results are to be obtained.

Somewhat later, this proposed method was used in a study of the comparative merits of a number of different kinds of corrosion tests carried out on the same metals in the same kind of solution.[2] Although the data secured were not extensive enough to warrant a

[1] W. Blum and H. S. Rawdon, Principles of Electrolytic Studies of Corrosion, Trans. Am. Electrochem. Soc., 52, p. 403; 1927.

[2] H. S. Rawdon and E. C. Groesbeck, The Effect of the Testing Method on the Determination of Corrosion Resistance, B. S. Tech. Paper No. 367; 1928.

definite recommendation concerning the use of the accelerated electrolytic test in preference to any other, the agreement, on the whole, of the results of this test with those of simple immersion was as good as was obtained with the other methods used. However, the results obtained in a few tests in which the corrodent had been saturated with nitrogen as a means of expelling any oxygen which might be present in the solution before the corrosion test was carried out, suggested that the results obtained in an accelerated electrolytic corrosion test may be markedly influenced by the condition of the solution with respect to the presence of oxygen or other gases.

The present study was carried out primarily with the aim of studying this effect in greater detail in order to show whether or not a careful control of the conditions, with respect to oxidation, under which the accelerated electrolytic test is carried out is necessary. Incidentally, it was also hoped that some information on the general subject of the effect of aeration on "submerged corrosion" (in particular, "anodic corrosion") might be gained.

Studies recently carried out by Tödt,[3] the results of which were available to the authors only after the present tests had been nearly completed, show that in the case of "couples" of dissimilar metals immersed in an electrolyte the magnitude of the current set up in any particular case is dependent in large measure upon the condition of the solution with respect to the access of oxygen (air).

II. MATERIALS AND METHOD

1. MATERIALS

Commercial copper and nickel in sheet form were the two metals used throughout. The specimens were cut from the same sheet as was used in the previous study.[4] A normal solution of sodium chloride was used as the corrodent throughout. In the experiments which involved the use of oxygen or nitrogen, gas of ordinary commercial purity was used.

2. METHOD

The method, which has already been described in detail,[5] consisted essentially in determining the loss of weight of a specimen of sheet metal used as the anode of an electrolytic cell with a cathode of the same material "facing" the anode on each side at a definite distance, 2.5 cm (1 inch). The assembled "cell" is shown in Figure 1. For purposes of reference, Figure 2 has been reproduced here from the previous report and shows a diagram of the complete set-up. In the

[3] F. Tödt, Corrosion and Residual Currents, Korrosion und Metallschutz, **3**, 37–38; 1928; Zeit. Elektrochem, **34**, pp. 586–591; 1928.

[4] See footnote 1, p. 375.

[5] See footnote 1, p. 375.

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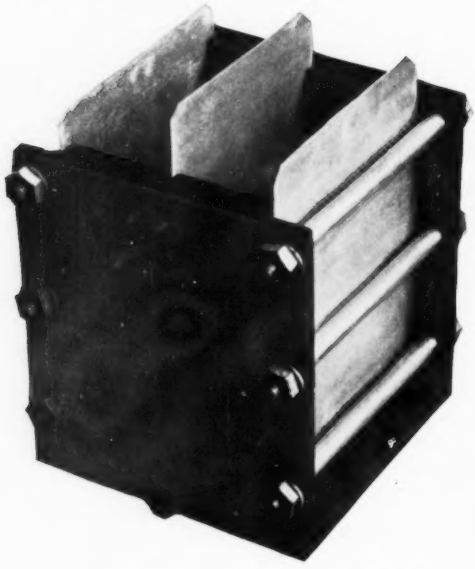

FIGURE 1.—*"Cell" used in the test*

previous work the cathode plates formed the ends of the cell and, of necessity, projected above the surface of the solution used, the volume of which (125 cm^3) was kept constant throughout the tests. In the present series of tests glass ends were used in the cell in order to permit the use of totally submerged specimens as well as partially submerged specimens. Only the latter were used in the previous tests. In all cases in which the specimens were fully submerged the surface area of the specimen was equal to that wet by the solution in the tests involving partial immersion. This was 25 cm^2.

The sodium-chloride solution was, for nearly all of the tests, prepared from distilled water which had been freshly boiled in order to

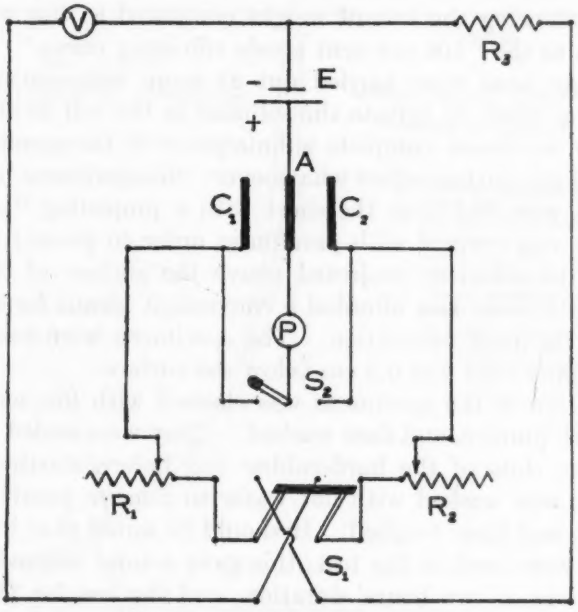

FIGURE 2.—*Electrical "set-up"*

render it gas free. In a few cases, however, the solution was intentionally prepared from distilled water with which no precautions had been taken to render it free from air. In a number of other cases the sodium-chloride solution, after being prepared from gas-free distilled water, was "charged" with oxygen or nitrogen by bubbling the gas through it. When it was desired to maintain an atmosphere of oxygen or of nitrogen above the solution the cell was inclosed beneath a bell jar through which a gentle stream of oxygen (or nitrogen) was passed and allowed to escape into the surrounding atmosphere.

In determining the effect of each variable studied a number of runs (usually four) was taken, the voltage applied being increased

for each succeeding "run" and the results expressed in the form of loss-of-weight-potential curves. As a basis of reference, curves have been included in this report which show the current densities produced at each potential under corresponding conditions. To facilitate comparison with the loss-of-weight curves, these current densities have been expressed in terms of the equivalent weights of the metals by assuming 100 per cent anode efficiency (as Cu^{I} and Ni^{II}). In short, these curves show the loss of weight calculated in accordance with Faraday's law for the current resulting from the applied potential, and the departure of the curves showing the observed losses of weight from these curves represents the departure from 100 per cent anode efficiency for the currents measured. For brevity, hereinafter, the curve showing the loss of weight computed in this way will be referred to as the "100 per cent anode efficiency curve."

All of the tests were carried out at room temperature, and no attempt was made to agitate the solution in the cell during the run.

In order to obtain complete submergence of the specimens—that is, to avoid any surface effect whatsoever—the specimens to be totally submerged were cut from the sheet with a projecting "tail." This tail, which was covered with paraffin in order to protect it from the action of the solution, projected above the surface of the solution several centimeters and afforded a convenient means for making the necessary electrical connection. The specimens were submerged so that the upper edge was 0.5 cm below the surface.

The surface of the specimens was cleaned with fine emery paper, rubbed with pumice, and then washed. They were sealed with paraffin into the slots of the hard-rubber box before starting a "run." The anode was washed with hot water to remove paraffin after the run, dried, and then weighed. It should be noted that both sides of the anode were used in the test; this gave a total surface of 50 cm^2. Each run was of two hours' duration, and the loss for 24 hours was calculated on the basis of this. In practically all of the tests the voltage was observed to fall gradually, and it was maintained at the initial value only by lowering slightly the resistance of the circuit at intervals during the run.

III. RESULTS

The different variables given consideration in the various tests carried out were as follows:

1. Degree of immersion—total, partial.
2. Condition of the solution with respect to dissolved gas—containing dissolved air, freed from dissolved air, containing oxygen, containing nitrogen.
3. Atmosphere above the solution—air, oxygen, nitrogen.

The results obtained are summarized graphically in Figures 3 to 8, inclusive, as loss-of-weight-potential curves. Curves showing 100 per cent anode efficiency have also been given as a convenient means of comparison and reference. These computed losses on the basis of Faraday's law were based on the assumption that copper passes into solution as Cu^{I} and nickel as Ni^{II}.

From the results given in Figures 3 and 4 it will be seen that no very marked differences resulted from total immersion and from partial immersion in solutions containing some dissolved air as compared with similar tests in solution which had been freed from dissolved air. The curves followed rather closely throughout most of

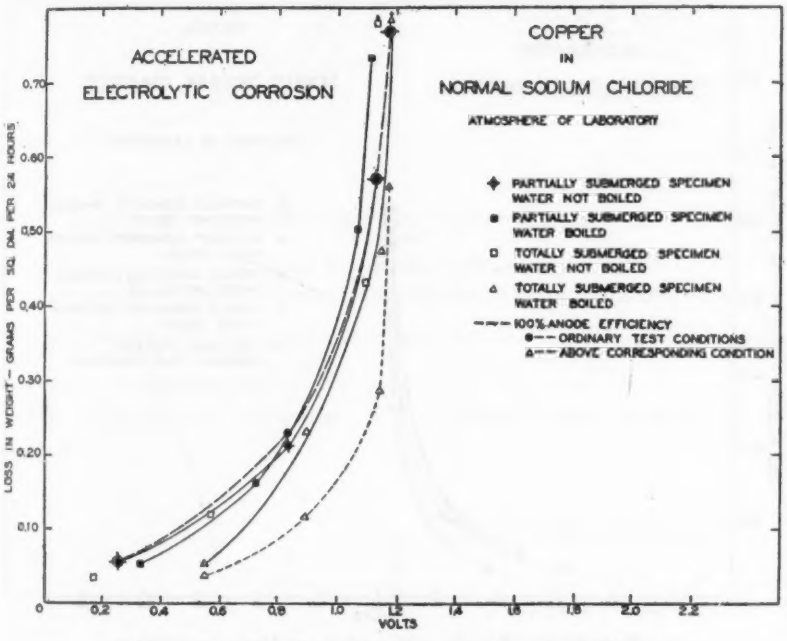

FIGURE 3.—*Results with copper—ordinary conditions*

their course that of the curve for 100 per cent anode efficiency for ordinary test conditions. The greatest divergence occurred with small anode losses; that is, low current densities. The most marked divergence from the curve showing 100 per cent anode efficiency was in the case of total immersion in a gas-free solution. It should be noted, however, that the curve showing 100 per cent anode efficiency under these conditions does not coincide with the other curve of this kind. In this particular case the observed losses were apparently greater than those indicated by the 100 per cent anode efficiency curve. The reason for this apparent anomaly is discussed later in the report. It should be noted that the current density for a given voltage—that is, the 100 per cent anode efficiency curves—varied some-

what according to the condition of the solution. For each curve, therefore, showing the relation between the applied voltage and the observed corrosion loss (loss of weight), a corresponding curve showing 100 per cent anode efficiency for the current produced by the applied emf may be drawn. In the following figures such curves have been drawn for those conditions which differ most widely.

It may be well to point out at this point that a fundamental assumption of the electrolytic corrosion test is that the corrodibility of a metal tested in this way is indicated by the potential necessary to produce a certain current density and, hence, a loss of weight. If the loss of weight is approximately that calculated by Faraday's law

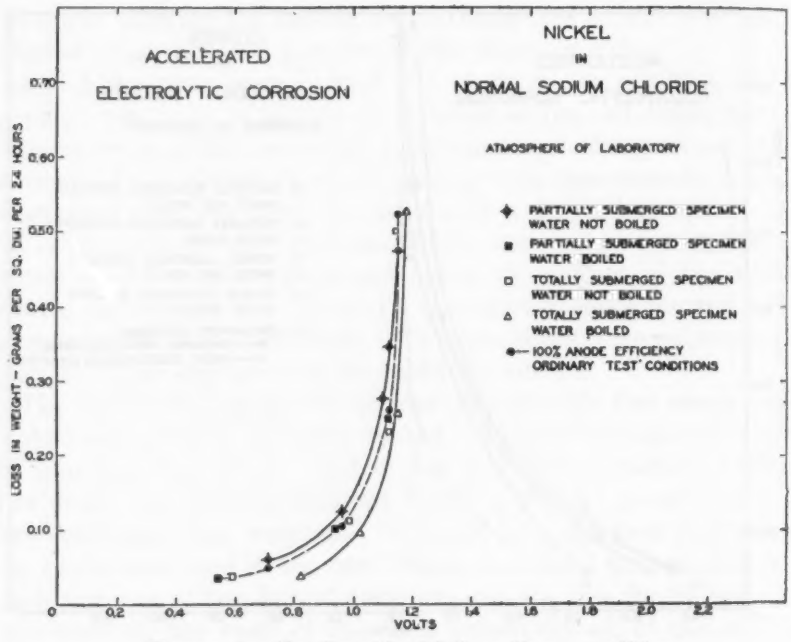

FIGURE 4.—*Results with nickel—ordinary conditions*

on the basis of the observed current, the "anode efficiency" is practically 100 per cent. The indications of the electrolytic test in such cases are not nearly so valuable as when the corrosion is very much less; that is, when the corroding anode shows a tendency to become passive. In those cases in which the anode corrosion is apparently greater than 100 per cent—that is, greater than the loss calculated by Faraday's law for the observed current—it is obvious that some other explanation must be sought. Thus, for example, it may be that the measured current does not represent the entire current which is contributing to the anode corrosion loss. "Parasitic" currents within the cell itself resulting from some nonuniform conditions often appear to be responsible.

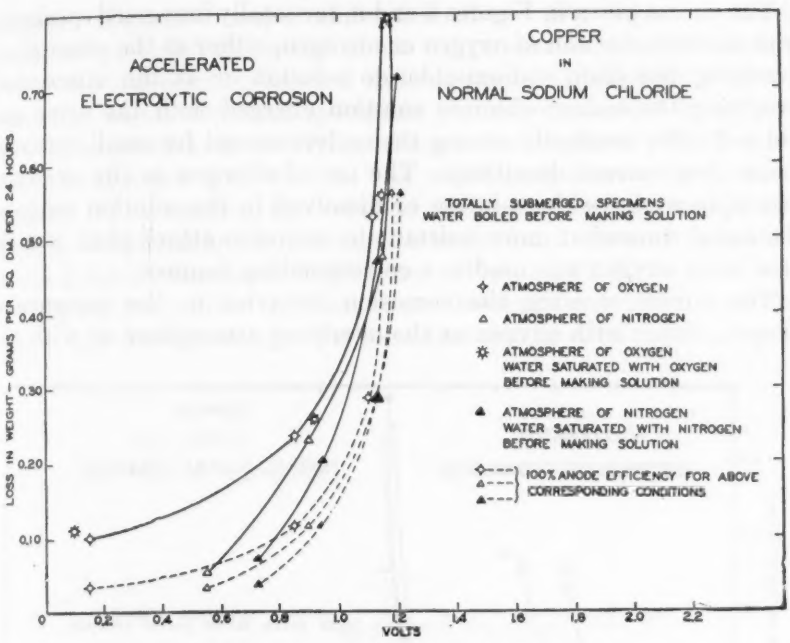

FIGURE 5.—*Results with copper*

Specimens were completely immersed and an atmosphere of oxygen or of nitrogen was used

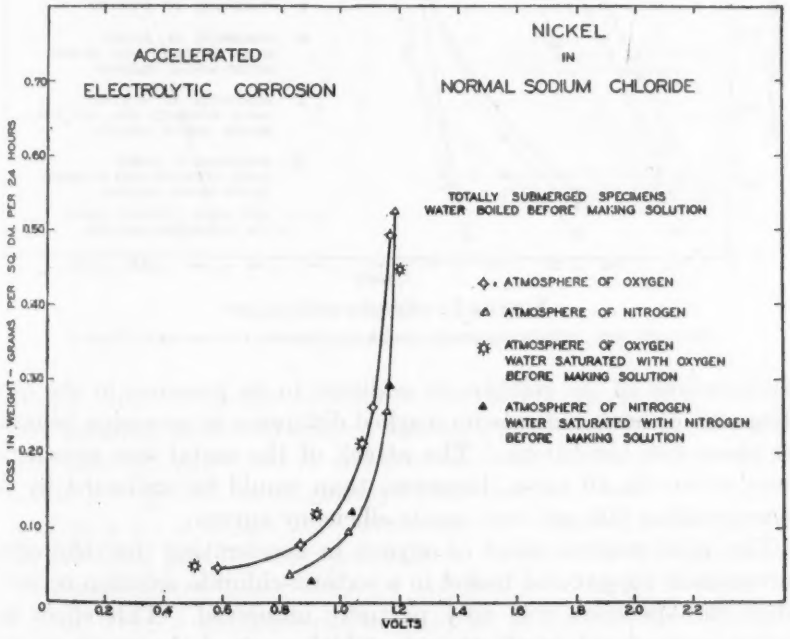

FIGURE 6.—*Results with nickel*

Conditions as in Figure 5

The curves given in Figures 5 and 6, for totally immersed specimens with the introduction of oxygen or nitrogen, either as the atmosphere overlying the plain sodium-chloride solution or as the atmosphere overlying the sodium-chloride solution charged with the same gas, did not differ markedly among themselves except for small corrosion losses (low current densities). The use of nitrogen as the overlying atmosphere above the solution or dissolved in the solution rendered the metal somewhat more resistant to corrosive attack than was the case when oxygen was used in a corresponding manner.

The curves showing the corrosion behavior in the presence of oxygen, either with oxygen as the overlying atmosphere or with this

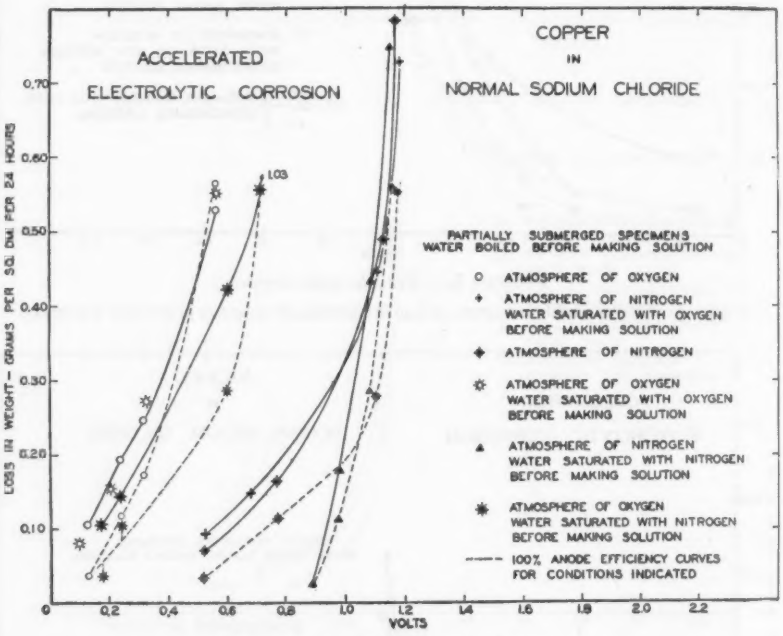

FIGURE 7.—*Results with copper*

Specimens were partially immersed; conditions, otherwise, the same as in Figure 5

gas dissolved in the solution in addition to its presence in the overlying atmosphere, indicate no marked difference in corrosion behavior for these two conditions. The attack of the metal was apparently more severe in all cases, however, than would be indicated by the corresponding 100 per cent anode efficiency curves.

The most marked effect of oxygen in accelerating the electrolytic corrosion of copper and nickel in a sodium-chloride solution occurred when the specimen was only partially immersed. This effect was rather pronounced in all cases in which part of the specimen was exposed to an oxygen atmosphere, regardless of whether the solution was initially "gas free," saturated with oxygen, or saturated with

nitrogen. Figures 7 and 8 show this effect. On the other hand, specimens partially immersed in an oxygen-saturated solution and having the upper part exposed in a nitrogen atmosphere behaved practically identically with specimens partially immersed in a "gas-free" solution with an overlying nitrogen atmosphere. In all cases in which nitrogen was used as the enveloping atmosphere or, in addition, for saturating the solution the corrosion behavior of the partially immersed specimens was quite similar to that of the corresponding totally immersed specimens. (Figs. 5 and 6.)

In Figure 9 are given typical curves showing the relation between voltage and current density for some of the runs made with copper.

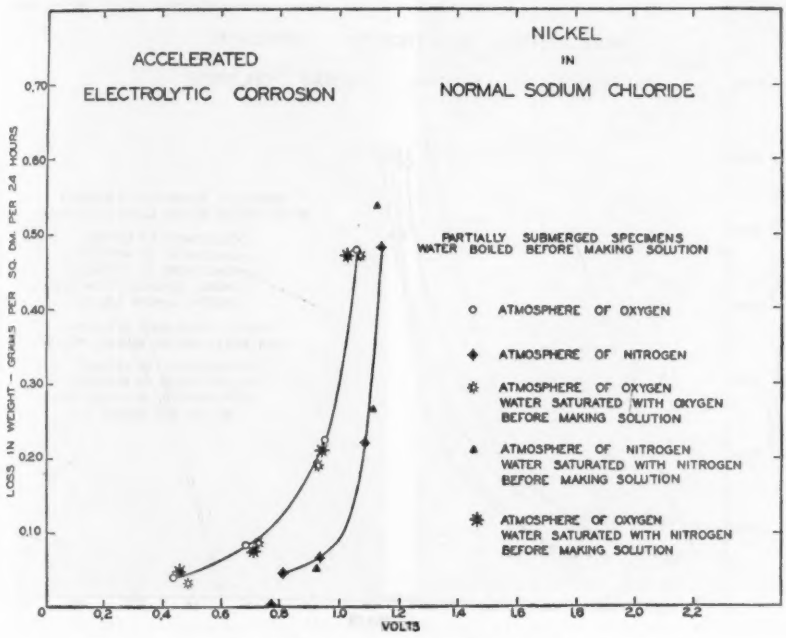

FIGURE 8.—*Results with nickel*

Conditions as in Figure 7

In reality these curves are the same as the 100 per cent anode efficiency curves inserted in the preceding figures, except that in these curves the currents are expressed in amperes, whereas in the other cases the equivalent weight of metal corresponding has been used.

In Figure 10 is shown the appearance of corroded copper anode surfaces—(*a*) a partially immersed anode corroded by the application of an external emf under ordinary conditions (that is, without the use of an oxygen atmosphere), and (*b*) an anode corroded similarly in an atmosphere of oxygen. It will be seen that in the former case the surface attack was uniform, whereas in the latter case it was not, the corrosive attack in a band across the anode surface adjacent to

the oxygen atmosphere being distinctly different from that over the remainder of the corroded surface. In order to render the anodic attack more distinct for inspection and photographic purposes, the solution in these cases was that which is used for the "ferroxyl" corrosion test. This solution, in addition to sodium chloride (10 g/liter), contained a small amount of potassium ferricyanide (2 g/liter) and enough agar-agar (4 g/liter) to cause the solution to "jell" upon cooling. A reddish-brown coloration (cupric ferrocyanide) on the anode, which is produced by the reaction with the ferricyanide of the copper as it passes into solution, gives a record of the uniformity in distribution of the corrosive attack.

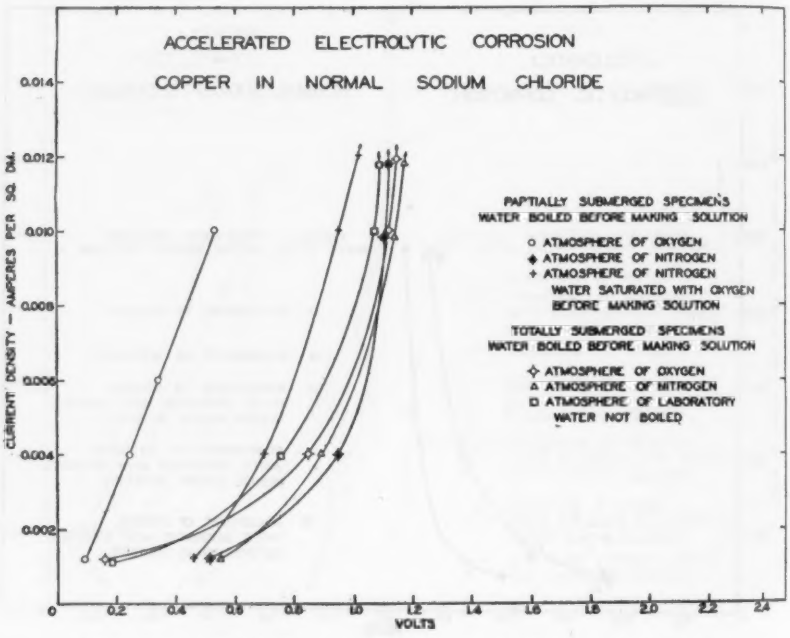

FIGURE 9.—*Typical current density—potential curves for copper*

A corresponding band across the cathode surface, just below the surface of the liquid, where the cathodic reaction was different from that over the remainder, was also observed when an oxygen atmosphere was used.

IV. DISCUSSION

The importance of the rôle played by oxygen in submerged corrosion under ordinary conditions is generally recognized. Indeed, as stated by Evans,[6] "Corrosion * * * by ordinary industrial waters, which are neutral or nearly neutral, requires the presence of oxygen." Advantage is taken of this fact, in a practical way, for the mitigation

[6] U. R. Evans, The Corrosion of Metals, p. 67; Edward Arnold & Co. (London); 1924.

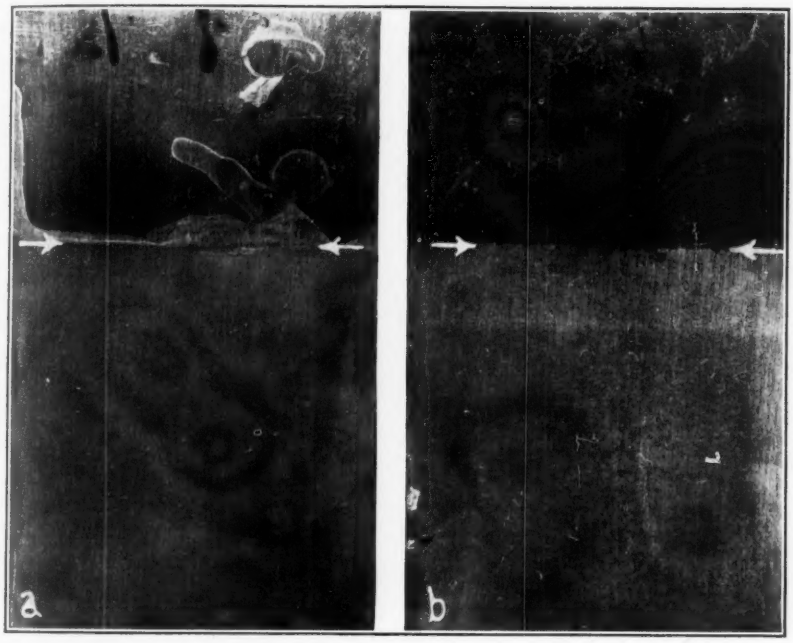

FIGURE 10.—*Appearance of the anode surface of copper corroded electrolytically in sodium-chloride solution*

(*a*) Under ordinary conditions; (*b*) with an overlying atmosphere of oxygen. The arrows indicate the "water line"

UNIV. OF MICH.

or prevention of corrosion in water-heating systems and the like, by removing the oxygen from the water before it enters the system. There is very little information available as to the possible corresponding effect of oxygen when the corrosive attack is accelerated electrolytically. It is evident, however, from the foregoing results that the effect of the presence of oxygen on electrolytic accelerated corrosion may be very pronounced. Especially is this true for those conditions which most closely approach those of "natural corrosion"; that is, low anode losses (low current densities). This discussion relates largely to results of this kind; that is, anode losses below 0.20 g (per sq. dm 24 hours) for copper and below 0.10 g for nickel. The fact that the foregoing results show that the presence of oxygen reduces the potential required in order to produce a given rate of corrosion may be taken as indicating, in general, the reliability of the electrolytic corrosion test when applied under conditions corresponding to given types of exposure.

The difference in the general nature of the results obtained when oxygen was used and those when oxygen was excluded by means of nitrogen (fig. 7) is very striking. The reason for this difference in behavior which first occurs to one is the "depolarizing" action of oxygen in the one case and the lack of it in the other. The results in this case illustrate very clearly the fact previously mentioned that there is no single "standard" based upon the Faraday loss which may be used for comparison of these widely varying results. It will be noted that the curves showing 100 per cent anode efficiency for the runs made under these varying conditions differ quite decidedly among themselves. The agreement between the observed corrosion losses and the corresponding 100 per cent anode efficiency curve was better. In practically all cases, however, the observed losses were greater than the calculated ones. Any loss in weight greater than that corresponding to 100 per cent anode efficiency is evidence that all of the current contributing to the corrosive attack was not measured; that is, some current flowed from one part of the anode to another part of the same as a result of some nonuniformity either in the metal or solution. A necessary and fundamental assumption of the electrolytic corrosion testing method is that a condition of uniformity does obtain. Except as these conditions are realized, the electrolytic test is "imperfect" and may be misleading. The present paper illustrates the importance and difficulty of fulfilling these conditions.

When oxygen was present in the solution its depolarizing action on the cathode surface may be considered as accounting, in part at least, for the greater corrosion losses which occurred as compared with the corresponding losses which occurred in solutions free from oxygen or containing only a relatively small amount. In order to explain

satisfactorily, however, the relatively high corrodibility when oxygen was used, particularly with specimens which were only partially submerged, it would seem that some additional cause must be sought. The effect of the uniform distribution of oxygen, which has been so ably demonstrated by Evans, appears to be an important factor in this regard.

As stated by Evans,[7] "An essential condition for the setting up of electrochemical action is some departure from uniformity." Variations in the oxygen distribution in the chloride solution with respect to the metal strips immersed therein would result in a change in the potential of certain portions of the otherwise uniform metal surface with respect to the solution. That part in contact with an oxygen-rich solution, such as the upper layer of the solution adjacent to an overlying oxygen atmosphere, would be cathodic in its behavior, whereas the portion of the same specimen bathed by solution having a lower oxygen content, anodic. This condition would, in itself, result in some electrolytic or corrosive action on a specimen.

A few experiments were carried out upon specimens of zinc, copper, and nickel in the manner described by Evans, to illustrate the fact that if two specimens of the same metal, connected electrically, are submerged at different depths in a solution so that one is exposed to more oxygen than the other, an emf is set up between the two. The metals, copper and nickel, when used in a sodium-chloride solution exposed to the atmosphere, behaved in the same manner as zinc under corresponding conditions, the behavior of which has been discussed in detail by Evans.[8]

The specimen near the surface of the solution hence, bathed by the solution of higher oxygen content was cathodic toward the one immersed deeper in the same solution; that is, in contact with a solution of lower oxygen content, as shown by potentiometer measurements as well as by use of a milliammeter. The measurement of the emf set up under these conditions is not at all a simple matter; the relatively high initial value observed rapidly drops as the experiment is allowed to proceed. Only qualitative tests were made to establish the fact that the behavior of the three metals was identical in their general behavior. Additional tests carried out under a bell jar and within an oxygen atmosphere showed that the magnitude of the emf set up was not greatly changed by the introduction of oxygen. The observations made on the uniformity of the corrosive attack of the anode (fig. 10) showed, however, that the area over which the differential-oxidation effect extended was decidedly increased by increasing the depth of the oxygen-rich surface layer of the solution.

[7] U. R. Evans, The Corrosion of Metals, p. 68, Edward Arnold & Co. (London); 1924.
[8] U. R. Evans, The Corrosion of Metals, p. 72, Edward Arnold & Co. (London); 1924.

If the potential of an immersed specimen, as a whole, is changed with respect to the solution by the application of an external emf—that is, raised (made an anode) or lowered (made a cathode)—the other condition which is the result of the nonuniformity in the oxygen distribution in the solution would be expected to remain unaltered. In effect, some portions of that specimen which, as a result of the external emf, is made to act as anode of the cell would be expected to be more reactive (more anodic) than would result from the external emf alone and, likewise, portions of the cathode of the cell somewhat more strongly cathodic than otherwise. On the other hand, it might be expected that areas which would be less reactive and less cathodic than would be indicated by the applied emf would exist on the anode and cathode, respectively. A somewhat analogous case would be expected to result from the use of electrodes which were nonuniform initially; for example, the use of electrodes of the same kind of metal which had been cold-worked over a portion of its length.

It will be seen from the curves that the effect of the use of an oxygen atmosphere was more pronounced than that alone of oxygen dissolved in the solution. The results obtained with partially immersed specimens when an oxygen atmosphere was used were practically identical with those obtained when, in addition to the oxygen atmosphere, oxygen was dissolved in the solution. The use of nitrogen in the solution with an overlying atmosphere of oxygen did not very materially lower the effect, since the condition of nonuniformity still obtained. The slight lowering of the corrosive attack in this case can, perhaps, be attributed to a lessening of the cathodic depolarization.

The most pronounced effect attributable to nonuniformity of oxygen distribution occurred in those cases in which partially submerged specimens were used. Undoubtedly, however, this differential-oxidation condition also obtains to some extent for totally submerged specimens and will account for the relatively higher corrosion losses obtained in oxygen-containing solutions. The specimens, completely immersed, were, of necessity, held vertically in the solution, the upper edge being 0.5 cm below the surface. On such a specimen the effect of nonuniform oxygen distribution would be expected to be more noticeable than on one immersed horizontally.

The most puzzling case of the entire series is the one in which the solution, which contained oxygen, was enveloped by an atmosphere of nitrogen. (Fig. 7.) Under these conditions the corrosion behavior of copper in sodium chloride agreed more closely with that obtained when nitrogen was used in the solution than the other cases with oxygen. If it is assumed that the two principal factors to be considered are the degree of cathodic depolarization and the auxiliary

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electrolytic effect resulting from the nonuniformity within the solution with respect to oxygen, it would seem that the latter in this case for some reason is less effective than the former. A clear and fully satisfactory explanation for this particular case is not yet forthcoming.

Consider now the results obtained when the tests were carried out, under ordinary conditions; that is, without the use of oxygen or nitrogen. (Figs. 3 and 4.) The variations in the test procedure consisted in the use of partially and of totally submerged specimens in solutions made from gas-free (boiled) water and from water which had not been boiled. It is evident that, in these cases, the effect which has been attributed to nonuniformity of oxygen distribution was practically negligible for the metals copper and nickel. At least it was not detected by the means employed in the test. With a more reactive metal, such as zinc, this might not be the case. The effect resulting from using a gas-free solution in some of the tests was quite marked and of sufficient magnitude to indicate that this factor should be taken into account. If the accelerated electrolytic corrosion test is to be used as a means for determining the relative corrodibilities of different metals, all the tests should be made with the same kind of solution; that is, with respect to the presence or absence of oxygen in the solution.

V. SUMMARY

Accelerated electrolytic corrosion tests on sheet copper and nickel in a sodium-chloride solution have been carried out by a method which has been previously described. Both anode and cathode in any one test were of the same metal, and the corrosion or anode losses have been expressed in the form of loss-of-weight-potential curves, together with the corresponding 100 per cent anode efficiency curves computed in accordance with Faraday's laws for the current which resulted from the applied emf's. The conditions with respect to oxidation were varied by inclosing the electrolytic cell in an oxygen or a nitrogen atmosphere, as well as by using a gas-free solution or one through which oxygen or nitrogen had been passed. The specimens were completely immersed in some cases and only partially in others. The results of the tests may be summarized as follows:

1. In general, only for small anode losses (low current densities) did the results of accelerated electrolytic corrosion tests, carried out in the manner used here, seem to have any real significance for the various conditions investigated. For higher current densities the loss-of-weight-voltage curves agreed quite closely with one another. Incidentally, however, it may be pointed out that the behavior in

electrolytic corrosion tests with low current densities would be expected to throw more light on the probable behavior under conditions of "natural" corrosion than would the behavior of the same metal with higher current density.

2. The results obtained with partially immersed specimens, especially when an oxygen atmosphere was used, differed quite materially from those with totally immersed specimens, the anode losses in the first case being decidedly greater than when the specimen was completely immersed, other conditions remaining unaltered.

3. The corrosion loss of partially immersed anodes with an overlying oxygen atmosphere was considerably greater than the corrosion loss of a totally immersed anode under the same conditions, except for very low current densities. By using a nitrogen atmosphere above the solution or by saturating the solution with nitrogen the corrosion losses on both totally and partially immersed anodes were reduced considerably; that is, a higher external emf was necessary in order to cause the same loss as occurred with lower voltages under the other conditions. The results confirm the reliability of the electrolytic corrosion test, at least to the extent of showing that the presence of oxygen reduces the potential required to produce a given rate of corrosion. Both copper and nickel behaved similarly in all respects under the different test conditions, the difference being more pronounced in the case of copper, however.

4. The differential-oxidation effect on a metal immersed in a solution, whereby the potential with respect to the solution of that part of the specimen which does not have free access to the air (oxygen) is rendered distinctly different (made anodic) from the potential of those parts of the same specimen having greater access to the air (cathodic), is believed to be associated with the relatively high corrosion losses obtained in many of the tests. This effect of differential oxidation originates within the "cell" and is to be considered as additional to that resulting from the application of an external emf to the cell. Examination of the corroded anode surface showed a distinct nonuniformity in the anode surface attack in those cases in which the differential-oxidation factor had been intensified (partial immersion in a solution with an overlying atmosphere of oxygen). The effect of oxygen in the solution as a "depolarizer" of the cathode surface and the absence of this effect when oxygen was excluded will account in large measure for the relatively low corrosion losses obtained when nitrogen was used. In practically all cases the observed corrosion losses were greater than those shown by the 100 per cent anode efficiency curve for corresponding conditions. It is obvious, therefore, that the entire current responsible for these losses was not measured. Currents set up as a result of potential differ-

ences resulting from some nonuniformity, either in the metal surface or in the solution, by reason of variations in oxygen concentration may account for these greater corrosion losses.

5. On the basis of the results of the present study, the accelerated electrolytic corrosion test can not, as yet, be considered a routine corrosion test. It is believed, however, that as a means of studying corrosion phenomena its value has been clearly demonstrated by the results of the study reported herein.

WASHINGTON, May 9, 1929.

REPRESENTATION OF ABERRATION DIFFRACTION EFFECTS BY MEANS OF ROTATING SECTORS

By A. H. Bennett

ABSTRACT

This paper describes a set of models constructed for the purpose of illustrating the combined effect of spherical aberration and out-of-focus conditions on the axial star image formed by any lens system of circular aperture. Representation of the star disks is accomplished by means of properly shaped rotating sectors. Figures are given showing sectors corresponding to cases in which the spherical aberration varies in amount from 1/8 λ to 1/2 λ. The effect of a change of focus in the presence of spherical aberration is illustrated.

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I. INTRODUCTION

In connection with the Michelson meeting of the Optical Society of America, held in November, 1928, at Washington, the writer exhibited a set of models, illustrating certain appearances of axial star images in the focal plane of an optical system of circular aperture, in which various amounts of spherical aberration were assumed to be present. In these models each star disk chosen for illustration is represented by a rotating sector such as is commonly used to obtain a symmetrical radial distribution of brightness.[1] These models were constructed for the primary purpose of presenting directly to the eye the combined effects of spherical aberration and out-of-focus conditions in displacing light from the central maximum of the diffraction pattern into the surrounding ring system of the star image.

It is well recognized that a study of the resultant effect of aberrations upon the diffraction pattern at the focus of any lens system requires a consideration of the wave theory of light and is of fundamental importance in determining the character of compensation that

[1] The application of the rotating sector in representing the image disk of a planet as seen through an ideal aberration-free telescope has been described by H. Seeliger, Bay. Akad. d. Wiss. Munchen, Sitzb. Math-Phys. Cl., 19, p. 404; 1896–1899.

has been attained in design and construction. Accordingly, for use in such investigations Rayleigh,[2] Conrady,[3] Buxton,[4] and Stewart[5] have deduced methods for evaluating the intensity distribution in the star image at and in the vicinity of the focus of a lens when the emergent wave front is distorted by the presence of aberration.

The set of models is of considerable interest in studying the formation and quality of images produced by optical systems because it affords a means for representing in concrete form the different intensity distributions in the diffraction patterns which result from selected values of the several geometric aberrations, together with given out-of-focus conditions. But it is believed that the models have a more general use in furnishing a means by which aberration diffraction effects, and the limitations thereby imposed on the definition, can be presented in tangible form to classes in physics. For this reason plates of the sectors have been reproduced from which it is a relatively simple matter to construct a set of models for the cases illustrated.

II. THEORY

The problem of determining the intensity distribution in the image of an axial point source in the focal plane of a lens having a circular aperture was first considered by Airy,[6] who showed that, with an ideally perfect objective lens entirely free from aberration, the distance between the central maximum and the first dark ring in the diffraction pattern subtends an angle of $\frac{1.22\,\lambda}{2\,r}$ radians at the objective, where λ is the wave length and r is the semiaperture of the lens.

Dawes,[7] in his measurements on double stars, experimentally showed that if two stars are to be resolved the minimum angular separation must be such that the central maximum of one image falls on the first dark ring of the other.

In practice, it is of importance to know the effect of the presence of aberrations on the definition produced by a lens or, in other words, the effect produced by distortion of an emergent wave front from its ideally spherical form.[8] Accordingly, Rayleigh in an extension of Airy's work considered the case of a lens possessing second-order longitudinal spherical aberration and concluded that, if the aberration introduces a phase difference of $\Gamma/4\ \lambda$ between the axial and marginal portions of the emergent wave front on arrival at the paraxial focal point, the definition of an object point is just noticeably impaired.

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[2] Lord Rayleigh, Phil. Mag., **8**, pp. 403–411; 1879.
[3] A. E. Conrady, M. N. R. A. S., **79**, pp. 575–593; 1918–19.
[4] Arnold Buxton, M. N. R. A. S., **81**, pp. 547–565; 1920–21.
[5] G. C. Stewart, Trans. Roy. Soc., London, Series A, **225**, pp. 131–198; 1926.
[6] G. B. Airy, Camb. Phil. Trans.; 1834.
[7] W. R. Dawes, Mem. Roy. Ast. Soc., **35**, p. 158; 1865.
[8] In order to determine the exact effect of various amounts of spherical aberration on resolving power, a miniature set of sectors, such as are described in this paper, has been constructed by the writer.

Conrady and later Buxton have extended the study of aberration diffraction effects to include all forms of spherical aberration. In addition to secondary longitudinal aberration, the higher orders were introduced and also the effects of a change of focus combined with the aberration were given consideration, since in most cases in the presence of aberration the paraxial focus is not the most favorable for producing greatest condensation of light in the central maximum of the star image. If one knows the total phase difference arising from change of focus, and from each of the several orders of spherical aberration, the intensity distribution in the star image can be computed.

By means of a trigonometric tracing of rays through a projected lens system, or by application of the Hartmann test to an actual lens, the longitudinal spherical aberration can be determined. Martin [9] has dealt with the method of transforming longitudinal spherical aberration to phase difference at any selected focus, and this transformation is in most cases the first step to be taken in determining the intensity distribution in axial images of point sources formed by any particular lens or system of lenses. Longitudinal spherical aberration can be expressed in the form

$$L = A_1 r^2 + A_2 r^4 + A_3 r^6, \text{ etc.} \tag{1}$$

where A_1, A_2, A_3, etc., are the constants for the longitudinal spherical aberration of the several different orders and r is the semiaperture. The phase aberration at the paraxial focus is

$$\eta = \frac{2\pi}{\lambda f^2} \int_o^r L\, r\, dr \tag{2}$$

where f is the image distance. At an axial point distant m from the paraxial focus the phase aberration is

$$\eta = -\frac{\pi m r^2}{\lambda f^2} + \frac{2\pi}{\lambda f^2} \int_o^r L\, r\, dr \tag{3}$$

The first term of the right-hand member of equation (3) represents the effect of displacing the focus to an axial point other than the paraxial focus, and it furthermore shows that by selection of a displacement, m, of suitable sign and magnitude the total phase difference for any particular case can be made a minimum.

Equation (3) can be written

$$\eta = \varphi_1 r^2 + \varphi_2 r^4 + \varphi_3 r^6, \text{ etc.} \tag{4}$$

in which the term in r^2 represents the effect of a change of focus, and the terms in higher even powers of r represent successively increasing orders of spherical aberration.

[9] L. C. Martin, Trans. Op. Soc. (London), **23**, pp. 63–92; 1921–22.

The intensity at any point in the star image has been expressed by Buxton in terms of the quantities of equation (4), the dimensions of the lens, and the position of the point under consideration, as

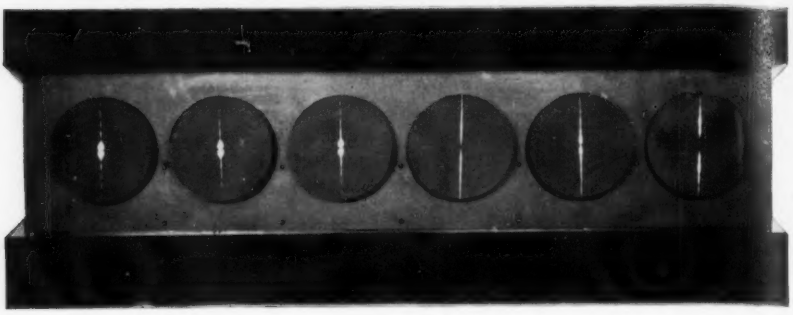
$$I=\left[\int_o^1 J_o\left(\frac{rx}{f}\right)\cos(\varphi_1 r^2+\varphi_2 r^4+\ldots)dr^2\right]^2 + \left[\int_o^1 J_o\left(\frac{rx}{f}\right)\sin(\varphi_1 r^2+\varphi_2 r^4+\ldots)dr^2\right]^2 \quad (5)$$

where r is the semiaperture; x, the radial distance of the point in the star disk from the axis; and f, the focal length of the lens. The intensity, I, can be computed by mechanical quadratures with the aid of tables given by Conrady for this purpose. In computing the intensities represented in the models, an extension of these tables was necessary, as it was desired to determine the intensity at points beyond the second bright ring in the star disk.

By the method outlined above the intensity distributions in several star disks, under various conditions of focus and in the presence of different amounts of spherical aberration, were determined.

III. CONSTRUCTION OF THE MODELS

After determining the intensity distribution for any particular combination of aberration and focus it is necessary to compute the outline of a sector which when rotated produces the desired distribution. Such a sector must be shaped so that at any radial distance from the center of the rotating disk the total angular width of the sectored portion is proportional to the intensity to be reproduced. This condition can be fulfilled by using any number of sectors on the same disk. A multisectored disk has the obvious advantage of requiring less speed of rotation for the avoidance of flicker than does a disk having but one sector. But, in order to reproduce relatively low intensities, it is necessary that the sectored portions be correspondingly narrow; and, with a multisectored disk, the individual sectors may become so narrow that it is difficult to avoid drawing them too wide in the regions where it is necessary to represent a brightness which approaches zero. By using two sectors on each disk, as shown in Figures 4, 5, 6, 7, 8, and 9, it is not difficult to attain the necessary speed of rotation for the avoidance of flicker, and at the same time the sectors do not become unduly narrow. It is mainly a matter of choice whether the sector is bounded on one side by a straight line radial to the disk or whether it is symmetrical about a radius of the disk. However, it was decided to bound the sectors by suitably shaped symmetrical curves because by so doing there is an increased probability of averaging out the accidental errors which occur in plotting and drawing the curved boundaries.



a b c d e f

FIGURE 1.—*Front elevation of apparatus*

The sectors when rotated simulate star disks formed by lenses having various amounts of spherical aberration.

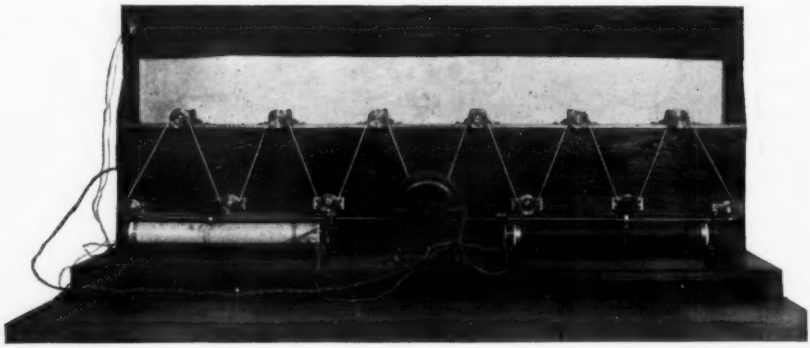
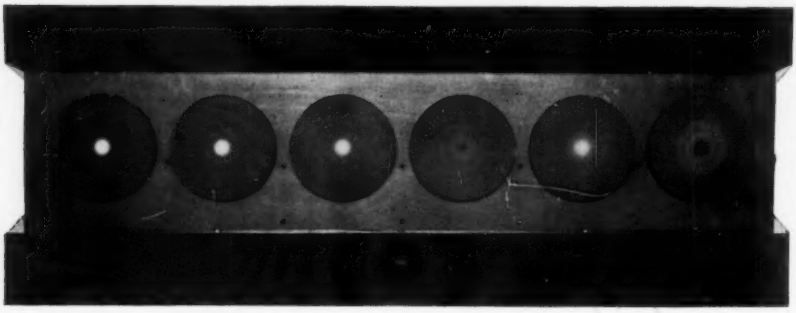


FIGURE 2.—*Rear elevation of apparatus showing method of driving the sectors*

By means of one long belt a single motor is used to rotate the six sectors simultaneously.



a b c d e f

FIGURE 3.—*Front elevation of apparatus showing sectors in rotation*

The sectors produce brightness distributions corresponding to the following cases: (*a*) Diffraction pattern for a perfect image, (*b*) diffraction pattern in the presence of ⅛ λ aberration, (*c*) diffraction pattern in the presence of ¼ λ aberration (Rayleigh limit), (*d*) diffraction pattern in the presence of ⅜ λ aberration with image plane displaced from paraxial focus in the direction from the caustic, (*e*) diffraction pattern in the presence of ⅜ λ aberration with image plane at paraxial focus, (*f*) diffraction pattern in the presence of ½ λ aberration with image plane displaced from paraxial focus in the direction toward the caustic.

UNIV. OF MICH.

In computing the intensities at the different points in the diffraction pattern by the method to which reference has been made the results are expressed in terms of the intensity of the central maximum of the ideal Airy disk. It is convenient to assign to this latter intensity a value of 100 per cent because it is the maximum relative intensity necessary to be reproduced by the sectors. With the intensities I so expressed, and with the assumption that the rotating disk contains two symmetrical sectors, at a distance r from the center of the disk the position of a point on the boundary of the sector can be expressed as

$$x = r \sin (I \times 90°)$$
$$y = r \cos (I \times 90°) \qquad (6)$$

the origin of the Cartesian coordinates being taken at the center of the disk.

For each of the cases illustrated in this paper a large-scale drawing was first made showing the sectors blackened. The finished disk is simply a photographically reduced negative print of the original drawing.

The sectors were mounted on the apparatus shown in Figures 1 and 2. The photographic print containing the sector was first mounted on a cardboard disk by means of mounting tissue. This, in turn, was attached (with hard wax) to a thin, flat brass disk. The sectors were mounted as described in order to give them sufficient flatness and rigidity to assure stability and freedom from vibration when rotated at high speeds. Each disk was mounted on a rotating spindle, with provision for adjusting the disk in its own plane so that the center of the figure accurately coincides with the center of rotation. The spindles project through a large blackened sheet of aluminum which provides a suitable background for the rotating sectors. Illumination is obtained by means of a number of automobile headlight bulbs in housings above and below the sectors.

IV. INTERPRETATION OF THE MODELS

In Figure 3, *a*, the perfect Airy star disk is illustrated and Figure 4 is the corresponding sector. As has been implied, the central maximum of this disk is considered as having an intensity of 100 per cent, whereas at the first dark ring the intensity decreases to zero. In the model it is, of course, impossible to avoid some reflection of light from the black portion of the disk, and consequently this ideal zero value is not quite attained. The effect of this scattered light is small, however, in comparison to the aberration diffraction effects which it is desired to represent and has been neglected in computing the shape of the sectors. The first bright ring has a maximum intensity of 1.6 per cent, while the intensity of the second bright ring

is only 0.4 per cent. As is shown later, the presence of aberration changes these intensities by amounts which are quite appreciable.

Figure 3, *b* (sector shown in fig. 5), represents the star disk at the paraxial focus of a lens which at that point imposes 1/8 λ phase difference between the paraxial and marginal portions of the wave front emergent from the lens. This phase aberration of 1/8 λ is half of the Rayleigh limit and is considered as producing no visibly deleterious effect on the star image formed by a lens. It is of interest to note the alteration in intensities in the star disk which this small amount of aberration introduces. The intensity of the central maximum is reduced to 95 per cent, the minimum intensity in the first dark ring is no longer zero but about 0.9 per cent, while the intensity of the first bright ring is increased to 1.8 per cent. Thus, the effect of the aberration is to decrease the intensity of the central maximum and to displace this light into the surrounding pattern. The effect is very slight, however, and it is very difficult in viewing the models to detect any difference between the contrast conditions in the perfect disk (fig. 3, *a*) and those of the 1/8 λ disk. This is in accord with the current idea that this amount of aberration can be tolerated in instruments of high quality.

In Figure 3, *c*, and also in the sector of Figure 6, the aberration has been increased to 1/4 λ which, according to Rayleigh, "begins to be decidedly prejudicial" to the definition. The intensity of the central maximum is now reduced to 80 per cent, with a further increase of illumination in the ring system and a consequent loss of contrast. Conrady suggests that this loss of contrast necessitates a more exacting tolerance of 1/6 or 1/8 λ in instruments of the highest quality.

The effect of spherical aberration of ½ λ in magnitude is shown in Figure 3, *e*, and the corresponding sector appears in Figure 7. Here the loss of contrast in the pattern is very pronounced, and a comparison with the ideal pattern Figure 3, *a*, reveals a pronounced deterioration of the quality of the image. On detail possessing sufficient contrast this amount of aberration does not, however, according to Conrady,[10] seriously affect the resolving power of a lens because the central condensation remains of about the same size as those of star images produced by lenses having much smaller amounts of aberration. Thus, such a lens might resolve double stars satisfactorily and yet not be suitable for resolving planetary or lunar details in which the contrast is weak.

Disks (*d*), (*e*), and (*f*) of Figure 3 and sectors of Figures 7, 8, and 9 compose a series designed to show the result of change of focus in the presence of spherical aberration, and they also serve to illustrate

[10] Dictionary of Applied Physics (London), 4, p. 221; 1923.

FIGURE 5.—*Sector representing star disk at paraxial focus of a lens having 1/8 λ spherical aberration*

FIGURE 4.—*Sector for representing Airy disk*

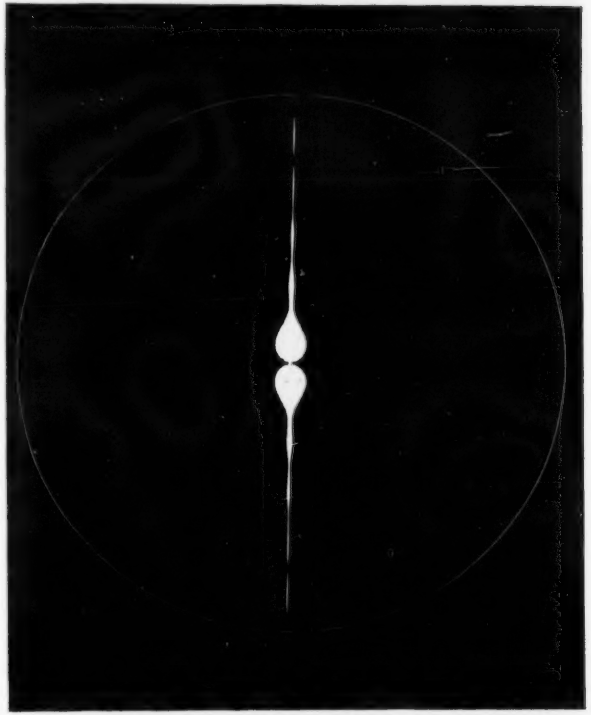


FIGURE 6.—*Sector representing star disk at paraxial focus in the presence of ¼ λ spherical aberration*

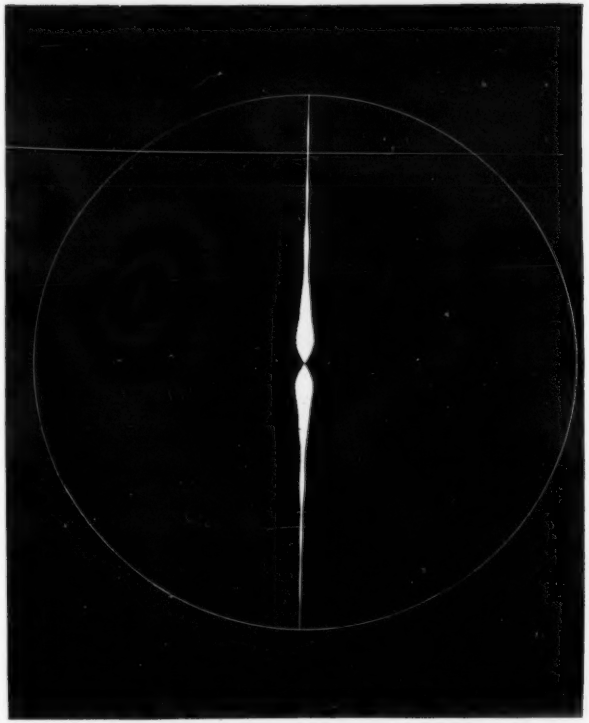


FIGURE 7.—*Sector representing star disk in the presence of ½ λ aberration at the paraxial focus*

in the presence of ¼ λ spherical aberration

of ½ λ aberration at the paraxial focus

230—3

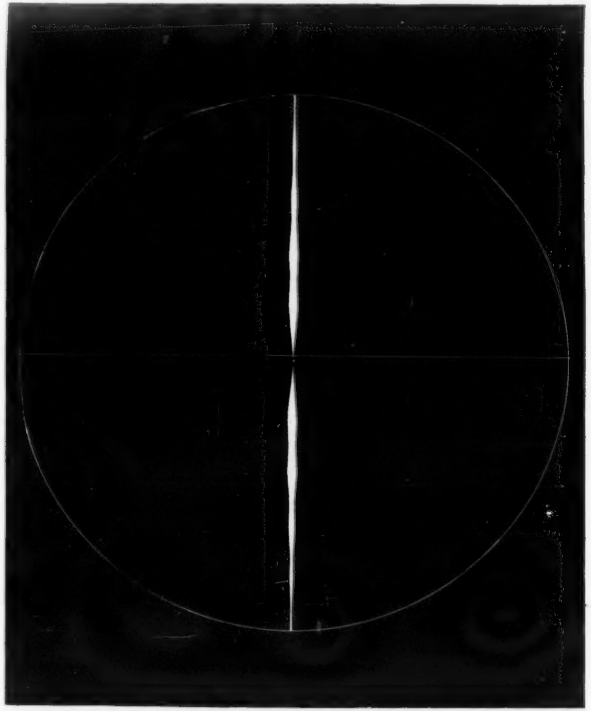


FIGURE 8.—*Sector for representing star disk in the presence of ½ λ aberration with image plane displaced in the direction from the caustic*

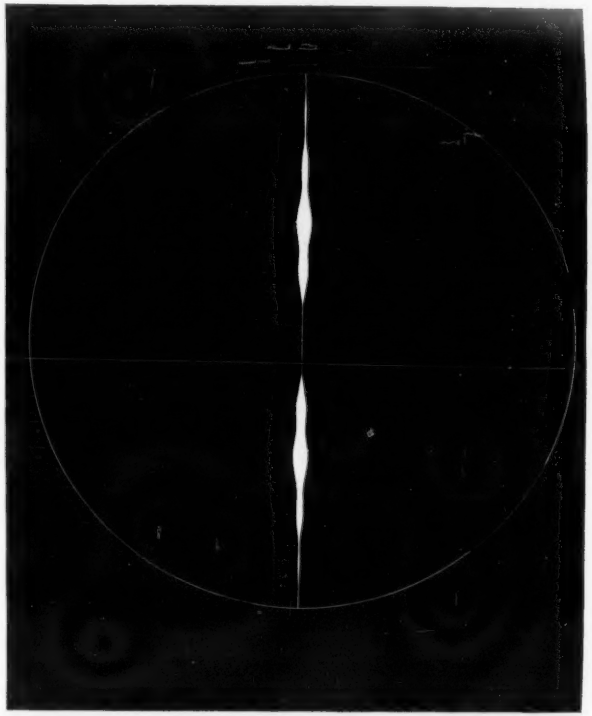


FIGURE 9.—*Sector for representing star disk in the presence of ½ λ aberration with image plane displaced in the direction toward the caustic*

an important method [11] of inspecting lenses for the presence of spherical aberration. If this defect is present, the rays, after refraction through a lens, do not pass through a single axial point but form the envelope of a surface called the caustic. If the caustic lies between the paraxial focus and the lens, the latter is under-corrected for spherical aberration, whereas in case of overcorrection the caustic is farther from the lens than is the paraxial focus. As a result of these conditions two cross sections of an emergent bundle of refracted rays, if taken to include axial points on opposite sides of the best focus, have characteristic appearances which are especially pronounced even in the presence of minute amounts of aberration.

Such appearances furnish a basis for the above-mentioned method of lens inspection which has not only the merit of high sensitivity but also that of convenience and simplicity. Let it be assumed that the star image formed by the lens is viewed through an eyepiece, as is the case with a telescope or microscope. If the eyepiece is racked from the best focus in a direction such that the cross section of the emergent bundle cuts the caustic, the out-of-focus star image is seen to consist of a sharply defined system of interference fringes. But if the eyepiece is racked away from the caustic the rings are very indistinct or even invisible.

For the case of the previously described star image of Figure 3, *e*, intensities were also computed for out-of-focus conditions at two positions along the axis on opposite sides of the paraxial focus. In each instance the displacement from the paraxial focus was such that the phase difference at the selected focus was 1λ, while, as previously mentioned, at the paraxial focus the phase difference is $1/2\lambda$. As a result the model shown in Figure 3, *f*, represents the image of Figure 3, *e*, when the latter is displaced from the paraxial focus in the direction of the caustic, while *d* represents the extrafocal image on the opposite side of the paraxial focus. An inspection of the sectors (figs. 8 and 9, respectively) shows that the contrast is stronger in the image displaced toward the caustic. This is easily noticeable when viewing the actual models; and, although it is hardly possible to reproduce photographically the small variations of contrast in the rotating sectors, the illustrations (fig. 3, *d* and *f*) show some difference in the appearance of these two out-of-focus images.

V. SUMMARY AND CONCLUSIONS

1. By means of models such as are described it is possible to represent directly to the eye the intensity distribution produced in a monochromatic axial star image formed by any actual or projected lens system.

[11] See H. Dennis Taylor, The Adjustment and Testing of Telescope Objectives, T. Cooke & Sons (Ltd.); 1921.

2. Interesting cases in connection with the theory and performance of optical systems can be demonstrated as, for example, the effects of various amounts of different orders of spherical aberration combined with effects of change of focus. The detection of spherical aberration by using infra and extra focal diffraction patterns is also illustrated.

WASHINGTON, April 6, 1929.

HOT AQUEOUS SOLUTIONS FOR THE QUENCHING OF STEELS

By H. J. French and T. E. Hamill

ABSTRACT

Surface and center cooling curves are given for small cylinders of high-carbon steel quenched in water, sodium hydroxide, sodium-chloride solutions, and oils at different temperatures. The characteristics of these cooling curves and a study of the hardnesses and structures produced suggested the possibility of using some of the hot aqueous solutions to bridge the gap between the cooling rates obtained with water and oils at atmospheric temperatures. Experiments with carbon and alloy steel tensile test specimens and gages seemed to justify the view that hot aqueous solutions can provide a useful group of coolants with graded cooling characteristics for the hardening of small steel pieces. Suggestions for further work are also given.

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I. INTRODUCTION

The experiments described in this report relate to the effect of temperature on the cooling properties of liquids widely used in the hardening of steels and comprise part of a general study of quenching which has been in progress for some time. The results previously reported have related to the properties and structures produced in carbon steels by different coolants at ordinary temperatures,[1] the effects of initial temperature and mass on center cooling,[2] the characteristics of center cooling curves,[3] and a study of the surface cooling of steels in quenching,[4] but little attention was given in these investiga-

[1] H. J. French and O. Z. Klopsch, Quenching Diagrams for Carbon Steels in Relation to Some Quenching Media for Heat Treatment, Trans. Am. Soc. Steel Treating, **3**, p. 251; 1924.

[2] H. J. French and O. Z. Klopsch, Initial Temperature and Mass Effects in Quenching, B. S. Tech. Paper No. 295; Trans. Am. Soc. Steel Treating, **9**, p. 33; 1926.

[3] H. J. French and O. Z. Klopsch, Characteristics of Quenching Curves, B. S. Tech. Paper, No. 313.

[4] H. J. French, G. S. Cook, and T. E. Hamill, Surface Cooling of Steels in Quenching, Trans. Am. Soc. Steel Treating, **15**, p. 217; 1929.

tions to the effects of coolant temperatures on the manner of cooling or the properties of the quenched steels.

This subject is of interest from several points of view. More information than is now available might point the way to further useful applications of different liquids and should help to establish the limits within which coolant temperatures should be controlled for uniform results; it should also serve to place the time-temperature relations, when quenching steels in hot liquids, upon a firmer foundation.

It is true that much is already known of the effects of temperature upon the coolants now ordinarily used in commercial heat treatment, but this information is of a general nature and based largely upon the properties and structures produced in different steels and the cooling characteristics at the interior of metal bodies. Quantitative information is lacking on the manner of cooling at the surfaces of steel bodies immersed in liquids at different temperatures, and it is the purpose of this report to present such data and a correlation of surface and center cooling with the properties and structures produced in steels.

As early as 1873 Caron [5] used water at 55° C. for the quenching of steel springs for hair triggers in rifles and obtained quite as good results as those obtained by more energetic quenching followed by tempering. He also used boiling water for the quenching of 0.2 to 0.4 per cent carbon steels to increase their tensile strength without altering their hardness.

II. METHODS OF TEST USED

The experimental methods already described [6] were used in the tests and the steel cylinders, one-half inch in diameter and 2 inches in length, were all quenched from 875° C. into coolants moving at 3 feet per second. The test cylinders were made of 0.96 per cent carbon steel having the chemical composition reported in Table 1.

TABLE 1.—*Chemical composition of the test cylinders*

[Steel C 41]

	Per cent
Carbon	0.96
Manganese	.28
Phosphorus	.016
Sulphur	.028
Silicon	.18

Washington City tap water was used in the water-quenching baths and in the preparation of the sodium-chloride brines and the sodium-

[5] E. Hitzel, Tempering by Warm Water and the Works of Lieutenant-Colonel Caron, Revue de Metallurgie Memoires, **12**, p. 584; 1915.

[6] See footnotes 1 and 4, p. 399.

hydroxide solutions. The two latter solutions were made, respectively, with ordinary table salt and technical sodium hydroxide, containing 96 per cent NaOH, 2 per cent Na_2CO_3, 2 per cent NaCl, and 2 per cent moisture. The concentrations referred to in this report are weight percentages, and the quenching was carried out in freshly prepared solutions.

Oil No. 2, which was used in a majority of the oil-quenching experiments, is a proprietary product and the same oil which was used in earlier experiments.[7] Its properties were approximately as follows: Specific gravity at 15° C., 0.874; flash point, 190° C.; fire point, 212° C.; initial boiling point, 375° C.; final boiling point, which is the equilibrium boiling temperature as determined in a reflux flask under atmospheric pressure, 375° C.; and final vapor temperature in the determination of the boiling points, 345° C. The exact composition of this oil is not now known, but analysis indicated that it is probably a mixture of a naphthene base (mineral) oil and about 3.3 per cent fatty oil.

Oil No. 1 is another proprietary quenching oil and its selection for a few experiments was due to its reported ability to cause rapid cooling at high temperatures. This oil consists of a mixture of a small amount of a heavy Pennsylvania residuum oil of high flash point with a special distilled Pennsylvania stock of low flash point. Its properties were as follows: Specific gravity at 15° C., 0.867; flash point, 193° C.; fire point, 216° C.; initial and final boiling points (reflux method), 380° C.; final vapor temperature in the determination of the boiling points, 355° C.

The reported values of hardness for the surfaces of the quenched cylinders are based on 10 tests along the length of the cylinder in the area meeting the direct flow of the liquid. The tests were made after removing about 0.005 inch of the metal from the surface by wet grinding to form narrow flat bands along the length of the cylinders. Center hardness was determined from three tests after cutting the cylinders in half under water spray.

III. RESULTS OF THE TESTS

1. CENTER AND SURFACE COOLING CURVES

Figures 1, 2, and 3 show the center and surface cooling of the steel cylinders immersed in water, No. 2 oil, 5 per cent sodium-hydroxide and 5 per cent sodium-chloride solutions at temperatures between 20° and approximately 100° C. Data for the No. 1 oil are given in Figure 9.

The highest coolant temperature, for water and the aqueous solutions, is given as 99.5° C. The practice employed was to heat the bath to 100° C., then remove the source of heat, and transfer the

[7] See footnote 1, p. 399.

tank containing the heated liquid to the quenching apparatus described in reports already referred to. Based on observations with the water baths, it was assumed that the average temperature drop in handling the different aqueous solutions was about 0.5° C., and the specified temperature, 99.5° C., merely indicates that the coolant temperature was slightly below the boiling point of water.

Figures 1, 2, 3, 4, and 9 show that increase in the temperature lowered the cooling rates and increased the cooling times in water and the two aqueous solutions while opposite effects were produced in center cooling by the two oils. The changes were small in the oils

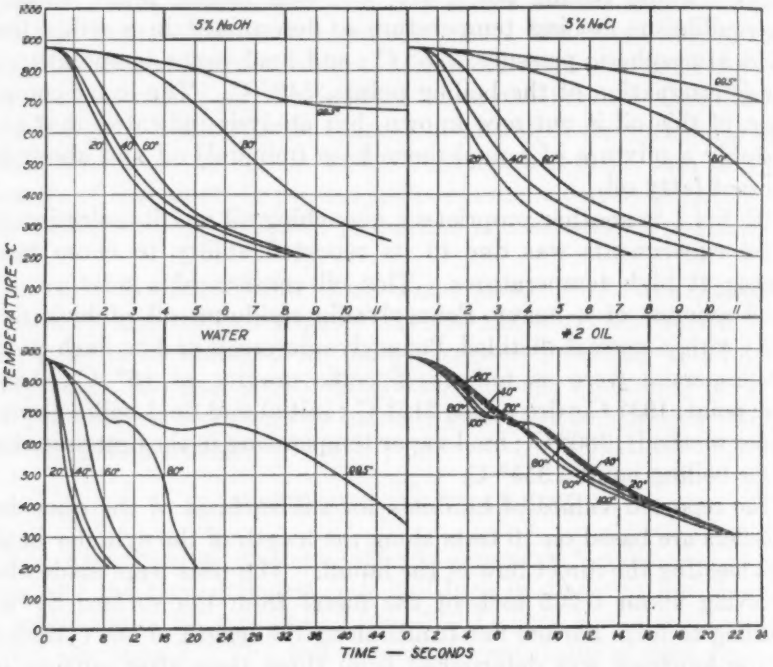

FIGURE 1.—*Center cooling curves of 0.96 per cent carbon steel cylinders quenched from 875° C. into liquids at different temperatures*

Coolant motion was 3 feet per second; cylinders were one-half inch diameter by 2 inches long. Each curve is the average of two or three tests.

throughout the entire temperature range studied (20° to 100° C.), and were not as marked between 20° and 60° C. in the water and aqueous solutions as between 60° and 99.5° C. Also, the changes in cooling times with increase in the coolant temperature were smaller in 5 per cent sodium hydroxide than in 5 per cent sodium chloride and, with the exception of the range 80° to 99.5° C., were smaller in 5 per cent sodium chloride than in tap water. (Fig. 4.)

The fact that temperature increase of the coolant affects the cooling in 5 per cent sodium hydroxide somewhat less than in water may be of distinct advantage in practical heat treatment, and probably con-

tributes in an appreciable degree to the rapidity of cooling in the sodium-hydroxide solution. In all quenching operations the liquid adjacent to the heated steel is raised in temperature even though it is only momentarily in contact with the heated metal surfaces. At least a part of the cooling of the steel is effected through contact with heated liquid and the vapors formed by or released from it.

In liquids which normally decrease in cooling speeds with rise in temperature a small temperature effect, as in the sodium hydroxide, means a tendency to maintain rapid cooling as well as ability to compensate for deficiencies in circulation which usually tend to raise the

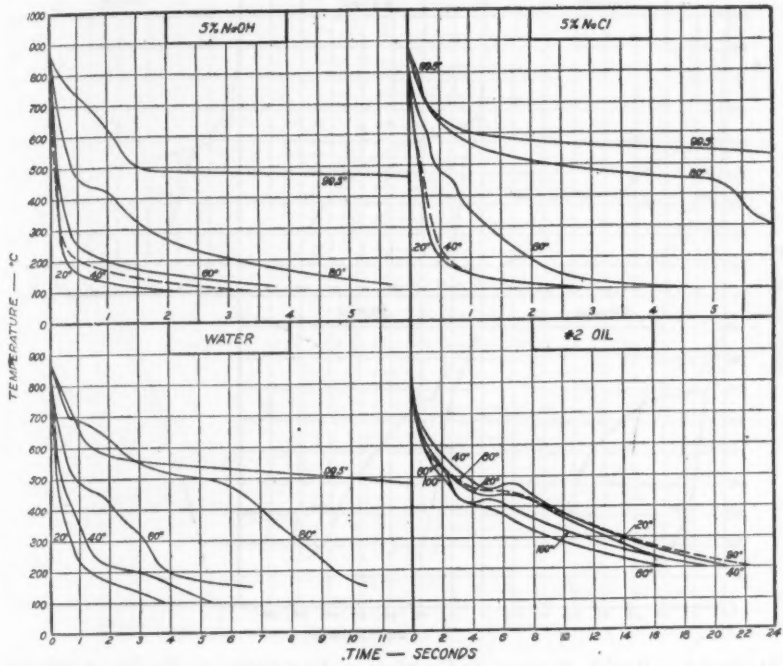

FIGURE 2.—*Surface cooling curves of 0.96 per cent carbon steel cylinders quenched from 875° C. into liquids at different temperatures*

Coolant motion was 3 feet per second; cylinders were one-half inch diameter by 2 inches long. Each curve is the average of two or three tests at a point meeting the direct flow of the liquid.

effective temperature of the quenching bath. From this viewpoint the 5 per cent sodium hydroxide is a more desirable coolant than water.

Figures 1 and 3 show that the center cooling of specimens immersed in water at 80° or 99.5° C. was somewhat more rapid at low temperatures around 200° to 300° C. than at high temperatures around 700° to 800° C. A similar condition was observed in 5 per cent sodium hydroxide at 99.5° C., but not at 80° C. nor in 5 per cent sodium chloride at 80° or 99.5° C.; in the last three cases the cooling rates were quite regular throughout the temperature range, 850° to 200° C. In general,

these center cooling characteristics were a reflection of the conditions at the surface, although the surface cooling became somewhat more irregular as the temperature of the aqueous solutions approached the boiling point of water.

Rapid cooling of the steel specimens at low temperatures in hot water and the hot aqueous solutions is well recognized and is usually considered to be disadvantageous, since steels are least able to deform without cracking at temperatures around 300° C., and so relieve the stresses accompanying the volume changes in hardening.

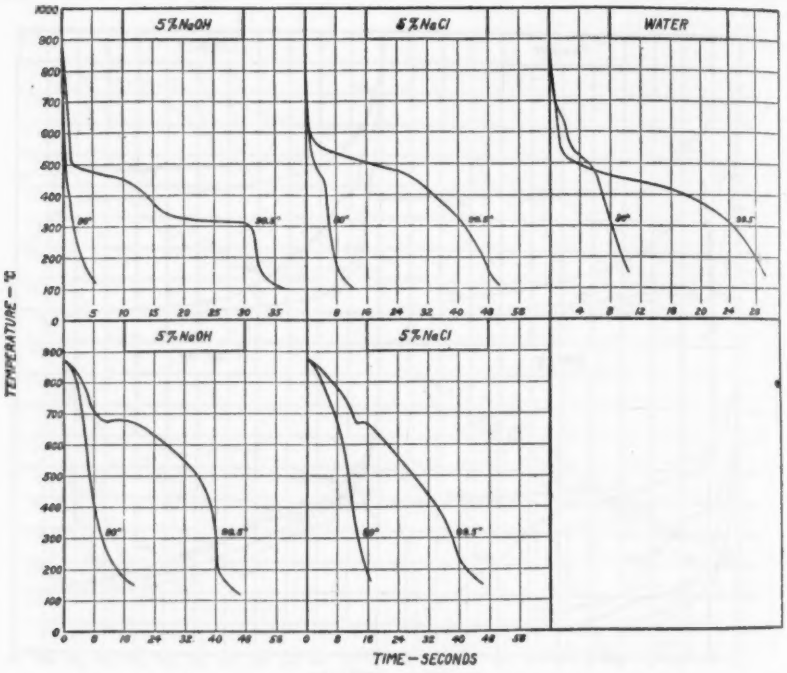

FIGURE 3.—*Replot of center and surface cooling curves in liquids at 80° and and 99.5° C. shown in part in Figures 1 and 2*

Surface cooling shown in top row, center cooling in bottom row.

However, it is difficult to see how the rapid cooling in hot water could, by itself, cause great difficulty, since the cooling rates are less than those obtaining in cold water, cold brines, and sodium-hydroxide solutions in which such difficulties are not important enough to prohibit their use in practical heat treatment. It seems more probable that the danger of cracking in hot water quenching is due to lack of uniform conditions over the surface of the steel during fairly rapid cooling at low temperatures. Evidence of nonuniformity was shown in the original records of the cooling curves, but a much better picture of this situation was obtained by watching and listening to the actual quenching operation.

As the initial temperature of the water bath is increased, somewhat less heat must be taken from the steel to form steam, and it is not unreasonable to assume that more steam will come in contact with, or become attached to, the surfaces of the metal in a given time. As has already been shown [8] such conditions promote nonuniform cooling, since the action at the contact surfaces between the metal and the coolant, or their products, is probably made up primarily of rapidly

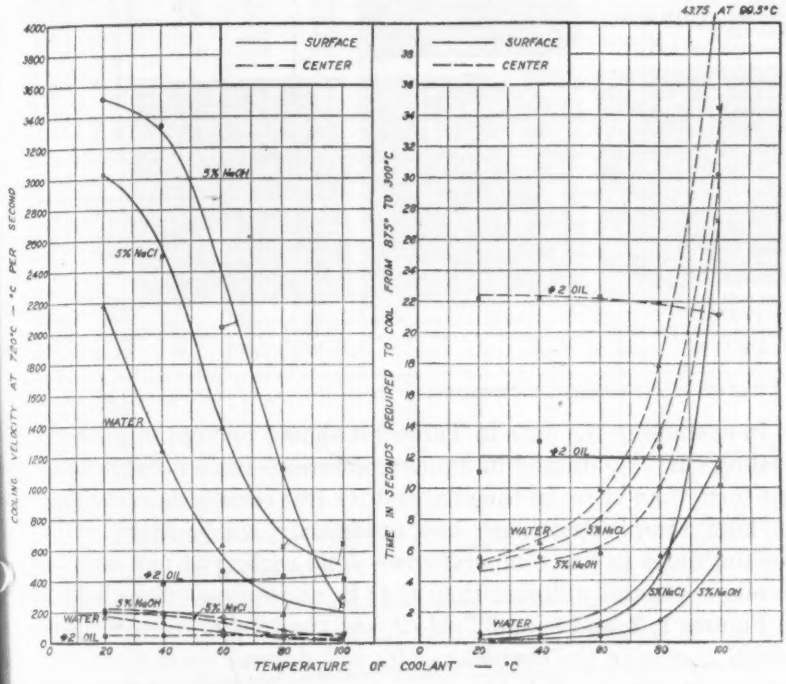

FIGURE 4.—*Effect of temperature on center and surface cooling times and rates in different liquids*

This is a summary of the curves shown in Figures 1, 2, and 3.

repeated cycles of steam generation, momentary attachment of steam to the metal surface and its removal.

In any case, hot water at temperatures in the neighborhood of 90° to 100° C. is not a good quenching medium under ordinary conditions. Where somewhat slower cooling is desired than can be secured in water at 20° C., and the oils are too slow, possibilities may be found in hot brines and, more particularly, in the hot sodium-hydroxide solutions. The center cooling curves were generally smooth without abrupt changes in direction for water at 40° C. and 5 per cent sodium hydroxide at 60° to 80° C. Also cooling times were obtained in the hot sodium-hydroxide solutions which were between water and oils at ordinary temperatures, as is shown in Table 2.

[8] See footnote 4, p. 399.

TABLE 2.—*Comparisons of hot water or hot aqueous solutions with oils at atmospheric temperatures in cooling high-carbon steel cylinders from 875° C.*

AT CENTER

Coolant	Approximate time, in seconds, to cool from 875° C. to designated temperature [1]					
	800° C.	700° C.	600° C.	500° C.	400° C.	200° C.
Water at 20° C	1.4	2.0	2.6	3.2	4.1	8.6
5 per cent NaOH at 60° C	1.6	2.2	2.8	3.5	4.3	8.8
Water at 40° C	1.6	2.3	3.0	3.9	4.8	9.4
5 per cent NaCl at 60° C	2.0	2.8	3.5	4.4	5.5	11.8
5 per cent NaOH at 80° C	3.4	4.8	6.0	7.1	8.3	14.1
No. 1 oil at 20° C	2.9	4.9	7.5	11.1	15.6	28.8
5 per cent NaCl at 80° C	3.9	7.1	9.4	10.9	12.1	16.0
No. 2 oil at 20° C	3.6	6.2	8.8	12.4	16.5	29.7

AT SURFACE

Water at 20° C	0.02	0.07	0.12	0.21	0.38	1.2
5 per cent NaOH at 60° C	.03	.08	.11	.15	.24	1.0
Water at 40° C	.06	.14	.22	.34	.56	2.0
5 per cent NaCl at 60° C	.03	.11	.22	.38	.62	1.8
5 per cent NaOH at 80° C	.07	.15	.25	.40	.72	3.1
No. 1 oil at 20° C	.07	.15	.34	.96	2.5	14.7
5 per cent NaCl at 80° C	.10	.30	.70	1.48	2.7	7.0
No 2 oil at 20° C	.09	.27	.89	2.4	5.5	19.3

[1] Heat effects of transformations disregarded.

In examining the data in Table 2 it should be kept in mind that the cooling curves obtained in aqueous solutions have a somewhat different form than those in the oils, and for this reason short cooling times at high temperatures are not necessarily concomitant with short cooling times to low temperatures. The cooling at low temperatures in oils is generally slower than that in aqueous solutions, as is shown in Figures 1, 2, and 3, and Table 2, and the temperature of the coolant which may give the desired results will depend upon the steel under treatment, its size and shape, etc.

2. HARDNESS AND STRUCTURES PRODUCED BY THE DIFFERENT COOLANTS

The effects of temperature of the coolant on the hardness and structures produced in the one-half inch diameter×2-inch cylinders of 0.96 per cent carbon steel are shown, together with cooling times, in Figures 5 to 9, inclusive. Figure 10 contains direct comparisons of the Rockwell hardnesses produced by quenching in the different liquids at different temperatures.

The fully hardened 0.96 per cent carbon steel, having a martensitic structure free from readily detectable areas of troostite, had a Rockwell "C" scale hardness of 63 to 65. This hardness was not attained at surface or center when the steel was quenched in either of the two oils, but was obtained at the center with water up to 60° C., 5 per cent sodium chloride up to 70° C., and 5 per cent sodium hydroxide up to 80° C. (Fig. 10.) With increase above the designated temperatures the hardness dropped appreciably and rapidly.

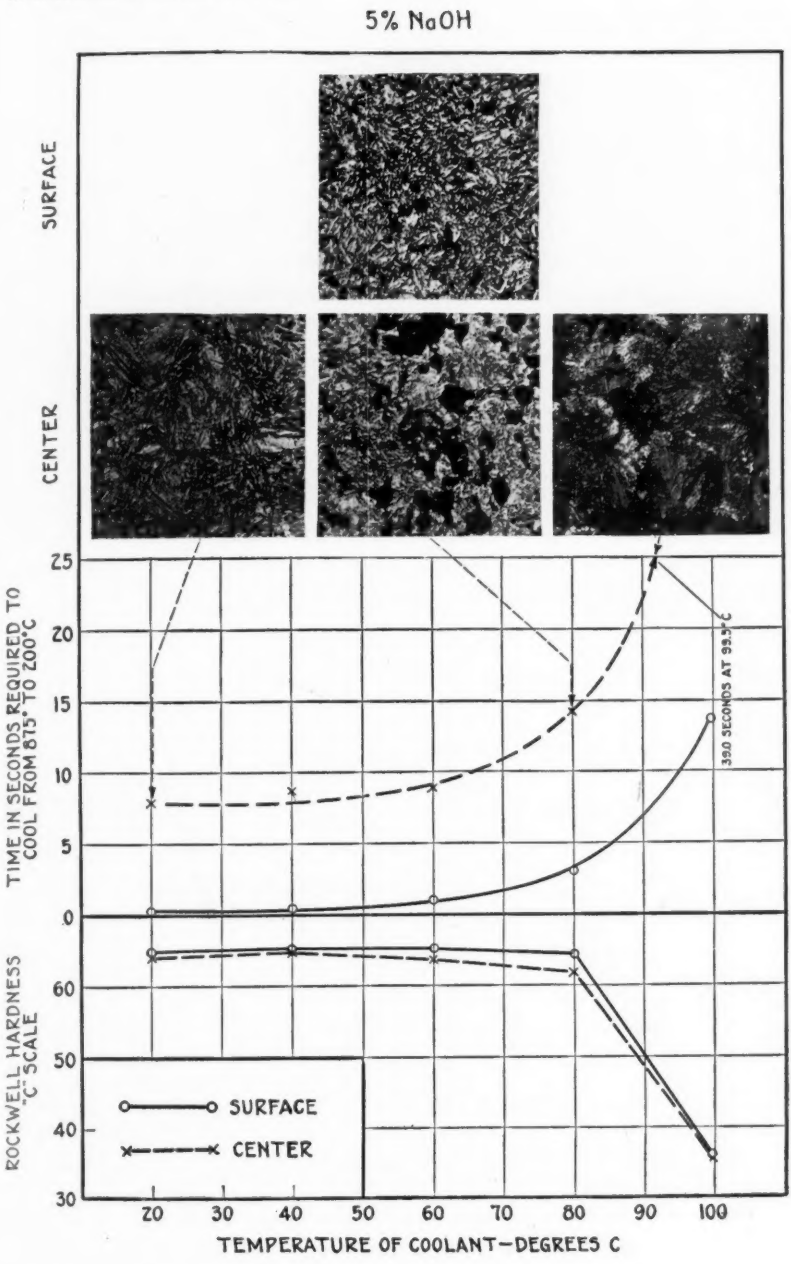

FIGURE 5.—*Hardness, cooling times, and structure at the center and surface of 0.96 per cent carbon steel cylinders quenched from 875° C. into 5 per cent sodium hydroxide at different temperatures*

Coolant motion 3 feet per second; cylinders ½ inch diameter by 2 inches long. Microstructures × 225; samples etched in 2 per cent HNO_3 in alcohol. Where surface structures resembled those at the center only the latter are given.

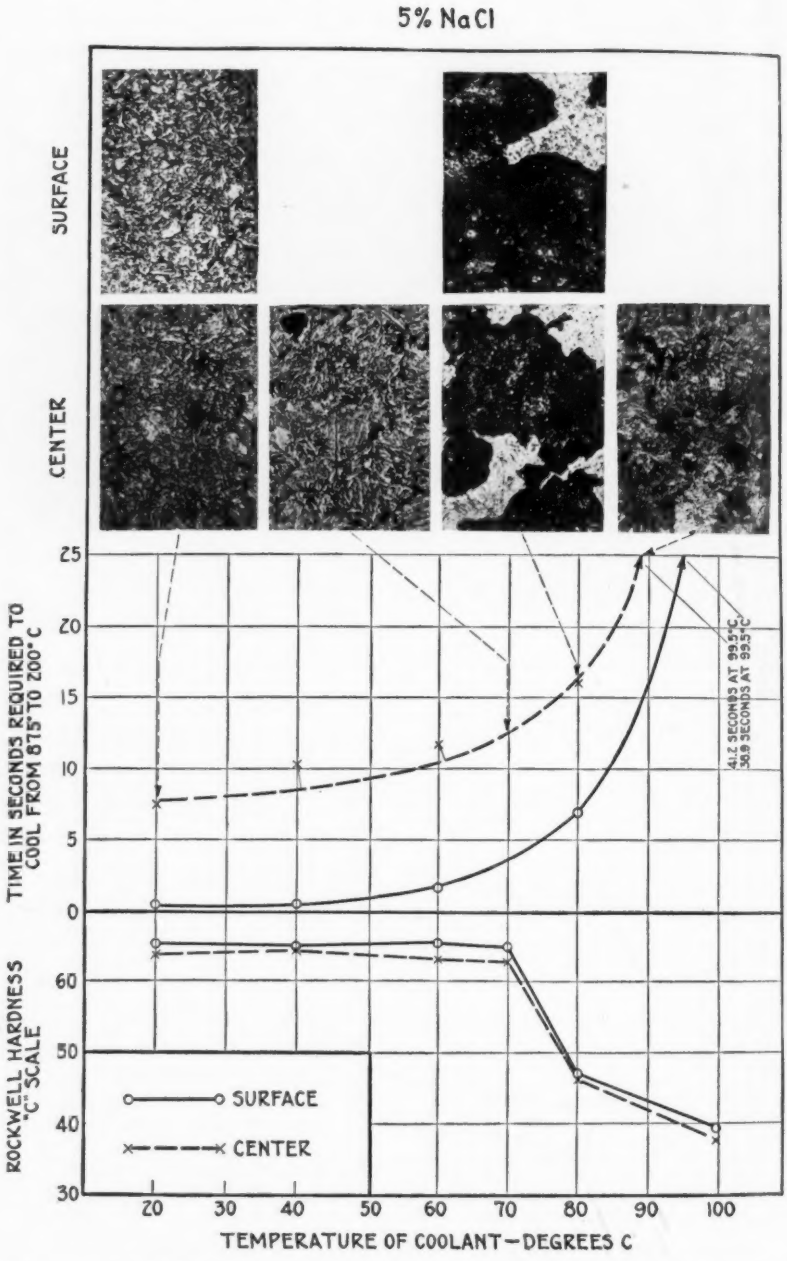

FIGURE 6.—*Hardness, cooling times, and structure at the center and surface of 0.96 per cent carbon steel cylinders quenched from 875° C. into 5 per cent sodium chloride at different temperatures*

Coolant motion 3 feet per second; cylinders ½ inch diameter by 2 inches long. Microstructures × 225; samples etched in 2 per cent HNO_3 in alcohol. Where surface structures resembled those at the center only the latter are given.

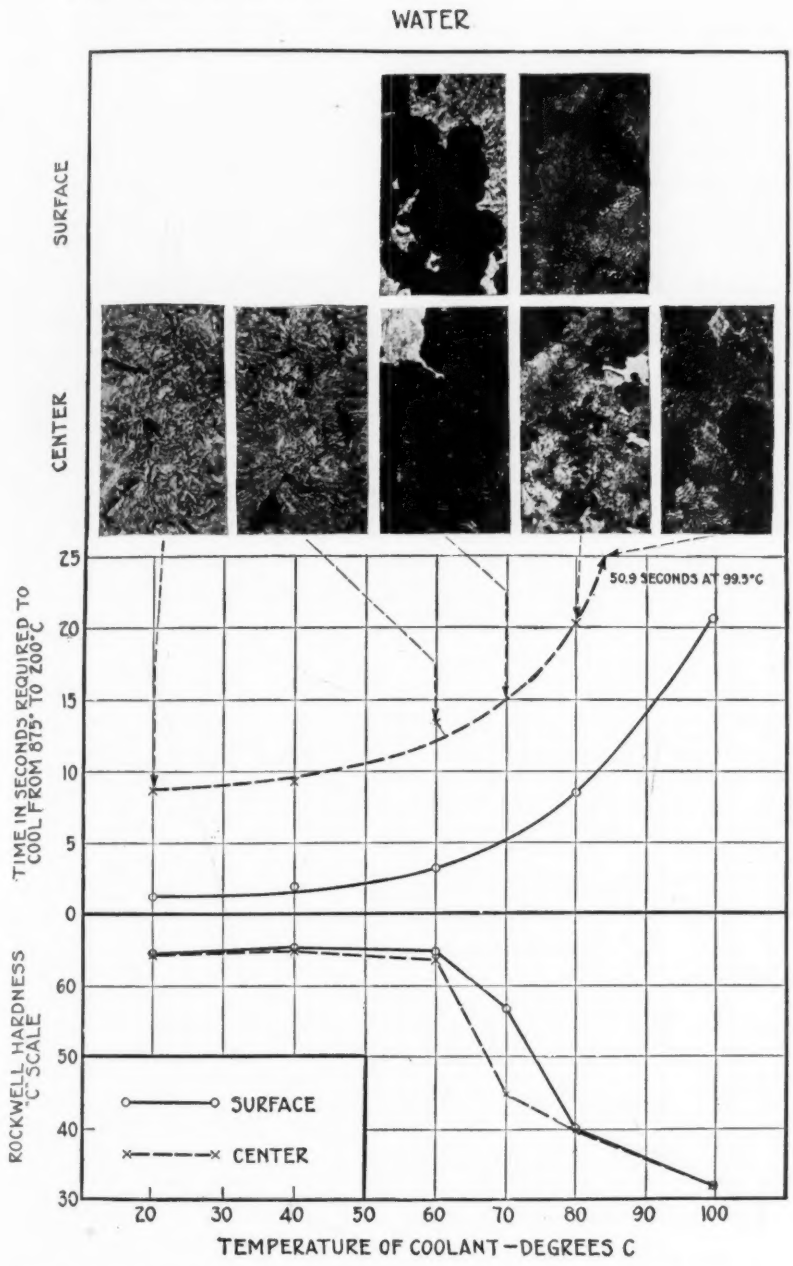

FIGURE 7.—*Hardness, cooling times, and structure at the center and surface of 0.96 per cent carbon steel cylinders quenched from 875° C. into water at different temperatures*

Coolant motion 3 feet per second; cylinders ½ inch diameter by 2 inches long. Microstructures ×225; samples etched in 2 per cent HNO_3 in alcohol. Where surface structures resembled those at the center only the latter are given.

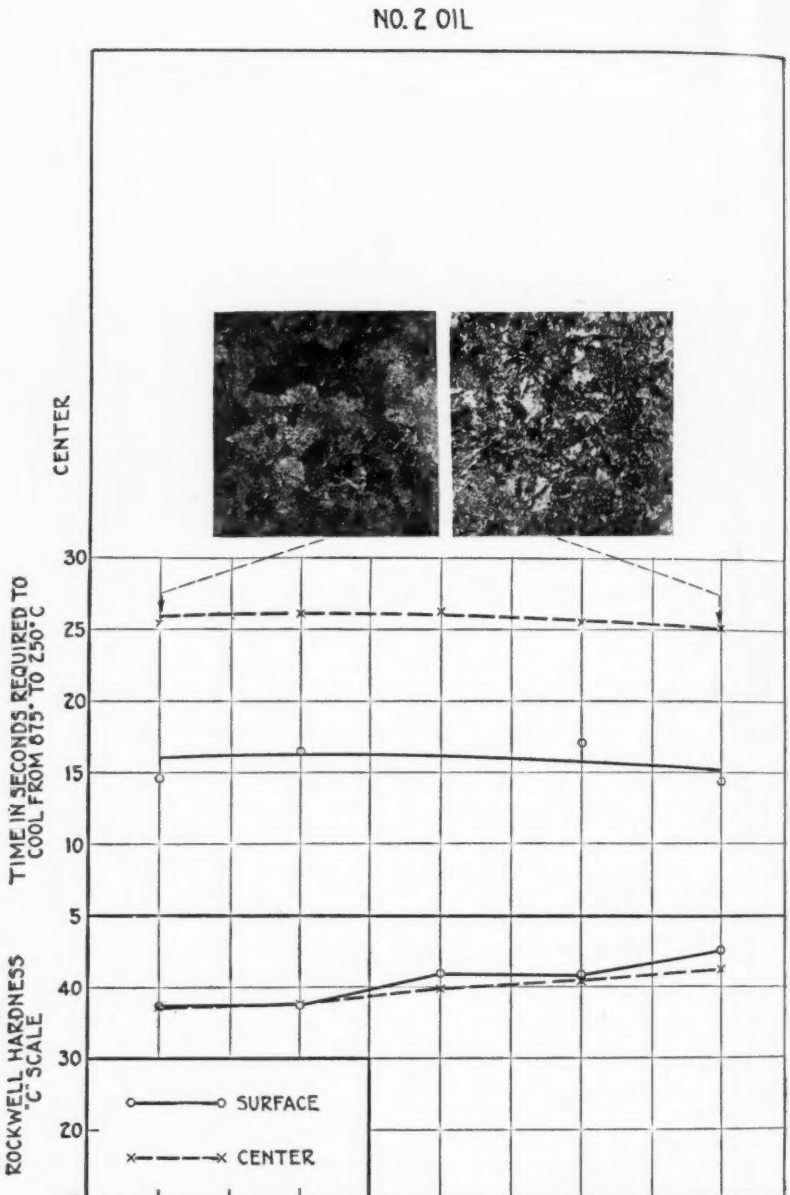

FIGURE 8.—*Hardness, cooling times, and structure at the center and surface of 0.96 per cent carbon steel cylinders quenched from 875° C. into No. 2 oil at different temperatures*

Coolant motion 3 feet per second; cylinders ½ inch diameter by 2 inches long. Microstructures × 225; samples etched in 2 per cent HNO_3 in alcohol. Where surface structures resembled those at the center only the latter are given.

While water at 60° C., 5 per cent sodium chloride at 70° C., and 5 per cent sodium hydroxide at 80° C. produced a Rockwell hardness equivalent to that obtained from the same coolants at atmospheric temperatures, there were appreciable differences in the structures of the quenched steels. In general, as the temperature of the coolant was increased, the structure changed from martensite (plus austenite) to martensite with increasing amounts of primary troostite, and finally to troosto-sorbite and sorbite with some evidence of lamellar pearlite.

Emphasis should be placed upon the fact that the hardness of the martensitic samples practically free from troostite was substantially

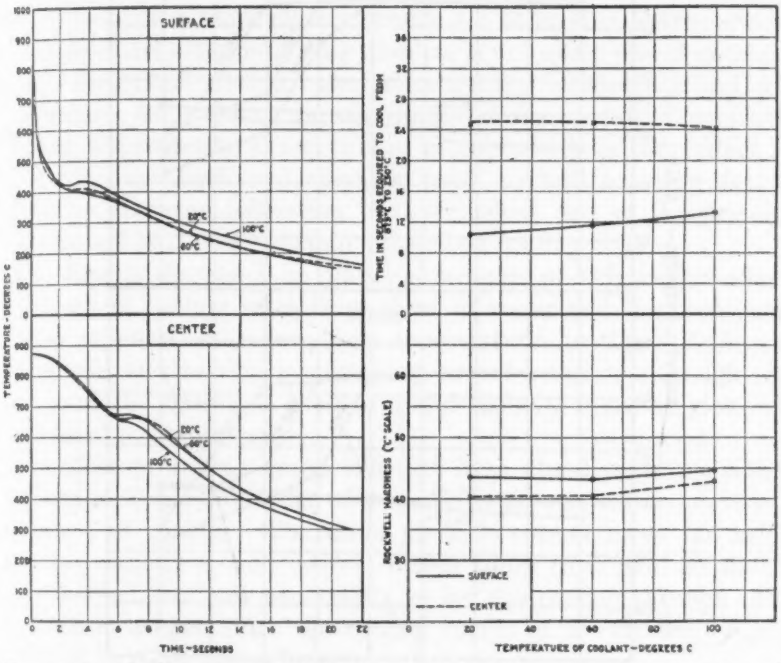

FIGURE 9.—*Cooling curves, cooling times and hardness at center and surface of 0.96 per cent carbon steel cylinders quenched in No. 1 oil at different temperatures*

Coolant motion 3 feet per second; cylinders ½ inch diameter by 2 inches long.

the same as that of the samples containing appreciable proportions of troostite. Hardness tests are frequently used in inspection to insure satisfactory heat treatment but may be inadequate when the properties desired are represented by martensite free from troostite.

Complete martensitization to the center of the one-half inch diameter cylinders was obtained only in the 5 per cent sodium-hydroxide solution at 20° C., whereas in previously reported tests [9] of a similar steel this was produced in water at 20° C. This difference may be ascribed to differences in the critical cooling rates of the two lots of steel;

[9] See footnote 1, p. 399.

that is, different cooling rates are required by different heats of steel of similar carbon content for the production of martensite free from troostite.[10]

As has been indicated already the effects of temperature of the coolant on the cooling of the steels quenched in oil were small but opposite to the effects observed in water and the aqueous solutions. The cooling was slightly faster in the No. 2 oil at 100° C. than at

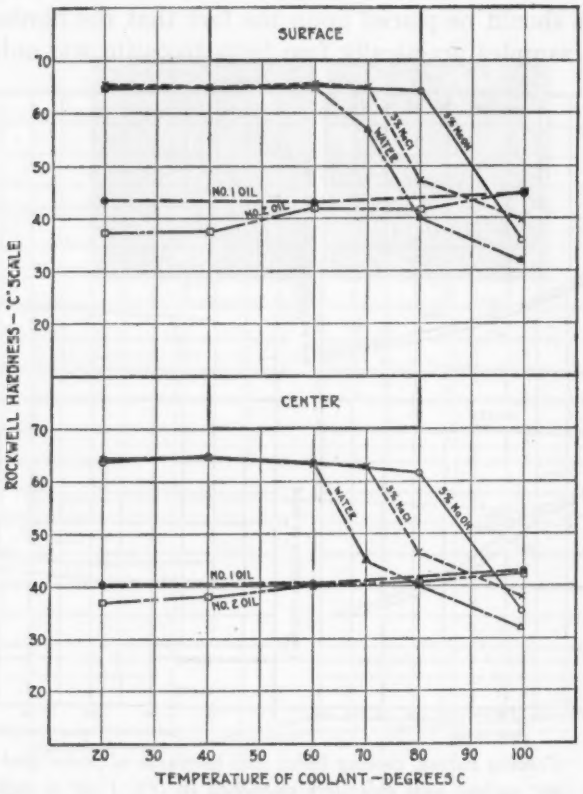

FIGURE 10.—*Surface and center hardnesses of the 0.96 per cent carbon steel cylinders quenched from 875° C. into different liquids at different temperatures*

Coolant motion 3 feet per second; cylinders ½ inch diameter by 2 inches long.

20° C. (figs. 1 and 2), and this was confirmed by the hardness tests reported in Figure 8. A similar result was shown in the No. 1 oil (fig. 9), but the changes were somewhat smaller. However, not all oils show increased speeds of cooling with increase in temperature[11] as in the two cases cited.

[10] General recognition of this is associated with the pioneer work on "abnormal" steels by McQuaid and Ehn, summarized along with more recent work in a paper by S. Epstein and H. S. Rawdon; Steel for Case-hardening—Normal and Abnormal Steel, B. S. Jour. Research, **1**, p. 423; 1928.

[11] J. A. Mathews and H. J. Stagg, Factors in Hardening Tool Steel, Trans., Am. Soc. Mech. Engrs., **36**, p. 845; 1914.

3. LIQUIDS WITH GRADED COOLING SPEEDS

Present-day hardening practice is based quite largely upon the use of oils, water, and the more rapid aqueous solutions, such as sodium-chloride brines, sodium-hydroxide solutions, and water sprays at ordinary temperatures. There is a large gap between the cooling rates obtained in the customary quenching oils and in water, and this is now usually taken care of by tempering subsequent to hardening or by interrupted quenching. Such procedure is entirely satisfactory for many practical purposes, but simplification and economy and possibly also technical advantages would result if coolants were available to provide a more closely graded set of cooling characteristics.

The practical solution of this problem is not solely one of obtaining certain prescribed cooling rates, since general availability and cost, permanence, safety from the standpoint of the operators, properties affecting adherence to the quenched metals which, in turn, affect the losses from the bath and cleaning costs, as well as other factors, should be given consideration. Nevertheless, one of the principal requirements is meeting certain prescribed cooling rates.

The liquids discussed in previous sections of this report offer a graded set of cooling rates from those of water and the more rapid aqueous solutions at atmospheric temperatures to those of the customary oils and in this respect they are of interest, although only some would be classed as good or useful coolants from the viewpoint of practical heat treatment.

The most promising group selected from the liquids considered are given in Table 3 in order of decrease in the speeds, or increase in the times, of cooling. The order given is correct in so far as the hardness, structures, and center cooling times from 875° to 200° C. are concerned, but not necessarily so for the cooling through other temperature ranges, since the cooling curves of the different liquids do not all have the same form.

A list based on somewhat closer gradations can be prepared from the data in Figures 1 to 10, inclusive, and substitutions can be made in a number of cases, but in Table 3 coolants showing the strongest tendencies toward irregular results have been omitted; only those were chosen in which smooth center cooling curves were obtained with fairly uniform slopes from 850° to 200° or 300° C.

The corrosive nature of the hot sodium-hydroxide solutions and the hot sodium-chloride brines is at the same time an advantage and a disadvantage. These solutions would not be easy to handle industrially from the standpoint of either equipment or operators, but the quenched steels are relatively free from heavy scale, and with bath temperatures of 60° to 80° C. or less will often come out bright. This denotes active scale removal during the quench, an effect which tends to promote uniformity in the results obtained.

TABLE 3.—*List of liquids given in order of decrease in cooling speeds*

Liquid and temperature	Cooling time from 875° to 200° C.[1] in seconds for—	
	Surface	Center
MORE RAPID THAN WATER		
5 per cent NaOH at 20° C	0.31	7.8
5 per cent NaCl at 20° C	.48	7.4
Water at 20° C	1.2	8.6
RATES BETWEEN WATER AND OILS		
5 per cent NaOH at 60° C	1.03	8.8
5 per cent NaCl at 60° C	1.8	11.8
Water at 60° C	3.2	13.4
5 per cent NaOH at 80° C	3.1	14.2
RATES CLOSE TO OR OF OILS		
5 per cent NaOH at 85° C	(5.0)	(17.0)
5 per cent NaOH at 90° C	(7.0)	(22.0)
No. 1 oil at 20° C	14.7	28.8
No. 2 oil at 20° C	19.3	29.7

[1] For 0.96 per cent C steel cylinders one-half inch diameter by 2 inches long; liquid moving at 3 feet per second.

Bracketed values estimated by interpolation.

Observations during the experiments clearly indicated that as the temperature of the sodium chloride and hydroxide solutions approached the boiling point of water there was a decided decrease in the uniformity of the conditions at the contact surfaces of the steel and the coolant. However, it should be kept in mind that all the experiments were made with low coolant velocities and that if better circulation were provided more uniform conditions could be expected. Liquids unsatisfactory at low rates of motion might become satisfactory at higher rates of motion.

4. TENSILE PROPERTIES PRODUCED BY THE HOT AQUEOUS SOLUTIONS

Two sets of tensile test bars were quenched in some of the hot aqueous solutions to give additional comparisons with water and the No. 2 oil at atmospheric temperatures. The first set was prepared from an oil-hardening nickel-chromium steel, while the second comprised specimens of 0.45 per cent carbon steel. The results of the tensile tests are summarized in Tables 4 and 5.

In the case of the nickel-chromium steel (Table 4) somewhat better uniformity was obtained in the two oil-quenched samples than in those which were quenched in water at 70° C., but the best combination of strength and ductility was obtained in samples quenched

in 5 per cent sodium hydroxide at 80° C. The results obtained with 5 per cent sodium chloride at 80° C. were not as good as those with the sodium hydroxide at 80° C., but as the temperature of the sodium hydroxide was increased to 85° and 90° C. there was a decrease in both the strength and ductility.

TABLE 4.—*Tensile properties of a Cr-Ni steel quenched from 840° C. (1,550° F.) into different liquids moving at 3 feet per second* [1]

(C, 0.23; Cr, 1.06; Ni, 1.64; P, 0.021; S 0.020)

Specimen No.	Coolant	Coolant temperature	Tensile strength	Breaking strength [2]	Elongation in 2 inches	Reduction of area	Type of fracture
		° C.	Lbs./in.²	Lbs./in.²	Per cent	Per cent	
5C-1	No. 2 oil	20	225,600	334,200	12.5	47.2	⅞ cup and cone, fibrous structure.
5C-2	do	22	225,000	321,400	12.0	44.1	⅞ cup and cone, fibrous structure.
Average			225,300	327,800	12.3	45.7	
5C-3	Water	70	246,000	308,000	9.0	33.1	⅞ cup and cone (deep elliptical), fibrous structure.
5C-4	do	71	232,400	358,000	12.0	49.0	Full cup and cone, fibrous structure.
Average			239,200	333,000	10.5	41.1	
5C-5	5 per cent NaCl	80	232,800	294,500	9.5	26.2	½ cup and cone (deep elliptical), fibrous structure.
5C-6	do	81	230,900	278,000	9.0	25.1	½ cup and cone (deep) fibrous structure.
Average			231,900	286,300	9.3	25.7	
5C-7	5 per cent NaOH	80	236,000	369,000	13.0	51.1	⅝ cup and cone, fibrous structure.
5C-8	do	80	235,500	361,500	13.0	50.0	Do.
Average			235,800	365,300	13.0	50.6	
5C-9	5 per cent NaOH	85	232,500	313,000	10.0	34.7	½ thin cup and cone, fibrous structure.
5C-10	do	85	230,800	301,000	9.5	30.2	⅝ thin cup and cone, fibrous structure.
Average			231,700	307,000	9.8	32.5	
5C-11	5 per cent NaOH	90	200,700	245,000	7.5	20.0	Sharp, rather flat break, fibrousstructure.
5C-12	do	90	198,800	243,500	6.5	20.0	Sharp flat break, fibrous structure.
Average			199,800	244,300	7.0	20.0	

[1] Specimens were held 30 minutes at temperature before quenching.
[2] The load at fracture divided by the area of the fractured section.

The specimens of 0.45 per cent carbon steel cracked when quenched in the 5 per cent sodium hydroxide at 80° C. (Table 5). Poor mechanical properties were obtained in the same liquid at 85° C., but when the temperature was raised to 90° C. an excellent combination of strength and ductility was obtained. Good strength, elongation, and reduction of area were also obtained in 5 per cent sodium chloride at 80° C., but erratic results were obtained in water at 70° C. Hankins

and Ford [12] tried unsuccessfully to quench 18-inch tensile specimens, 3 inches wide and three-eighths inch thick, of a 0.60 per cent carbon steel from 800° C. into water at 50° C. without cracking after being successful with 3 and 6 inch plates of the same width and thickness.

TABLE 5.—*Tensile properties of a 0.44 per cent carbon steel quenched from 815° C. (1,500° F.) into different liquids moving at 3 feet per second* [1]

(C, 0.44; Mn, 0.81; P, 0.025; S, 0.022)

Specimen No.	Coolant	Coolant temperature	Tensile strength	Breaking strength [2]	Elongation in 2 inches	Reduction of area	Type of fracture
		° C.	*Lbs./in.²*	*Lbs./in.²*	*Per cent*	*Per cent*	
7A-1	No. 2 oil	18	128,500	135,200	1.5	4.7	Fine crystalline structure, sharp break.
7A-2	do	21	148,500	158,000	1.0	5.9	Do.
Average			138,500	146,600	1.3	5.3	
7A-3	Water	70	106,500	111,500	3.0	4.5	Do.
7A-4	do	70	127,200	198,800	14.0	54.8	⅛ deep cup and cone, fibrous structure.
Average			116,900	155,200	8.5	29.7	
7A-5	5 per cent NaCl	79	119,200	189,300	17.0	47.2	⅝ deep cup and cone, fibrous structure.
7A-6	do	81	118,500	201,000	17.5	51.7	Do.
Average			118,900	195,200	17.3	49.5	
7A-7	5 per cent NaOH	80	Both specimens cracked in quenching				Very fine crystalline structure, sharp break.
7A-8		80					Very fine crystalline structure, rather sharp break.
7A-9	do	85	77,500	80,800	1.0	4.0	Very fine crystalline structure, sharp break.
7A-10	do	85	95,700	98,700	1.0	2.8	Very fine crystalline structure, rather sharp break.
Average			86,600	89,800	1.0	3.4	
7A-11	5 per cent NaOH	90	114,700	200,000	20.5	55.3	¾ cup and cone, fibrous structure.
7A-12	do	90	114,700	195,600	20.5	54.2	⅝ cup and cone, fibrous structure.
Average			114,700	197,800	20.5	54.8	

[1] Specimens were held 30 minutes at temperature before quenching.
[2] The load at fracture divided by the area of the fractured section.

The structures of some of the tensile-test specimens are shown in Figures 11 and 12. The No. 2 oil at 20° C. and the 5 per cent sodium hydroxide at 90° C. produced a troosto-sorbitic structure in the 0.45 per cent carbon steel, while the 5 per cent sodium chloride at 80° C. and the 5 per cent sodium hydroxide at 85° C. produced a martensitic structure containing appreciable proportions of troostite. The differences in ductility and tensile strength in samples 7A–9 and 7A–5 (fig. 11) were probably due in part to differences in the degree of

[12] G. A. Hankins and G. W. Ford, The Mechanical and Metallurgical Properties of Spring Steels as Revealed by Laboratory Tests. A paper to be presented before the 1929 spring meeting of the British Iron and Steel Institute.

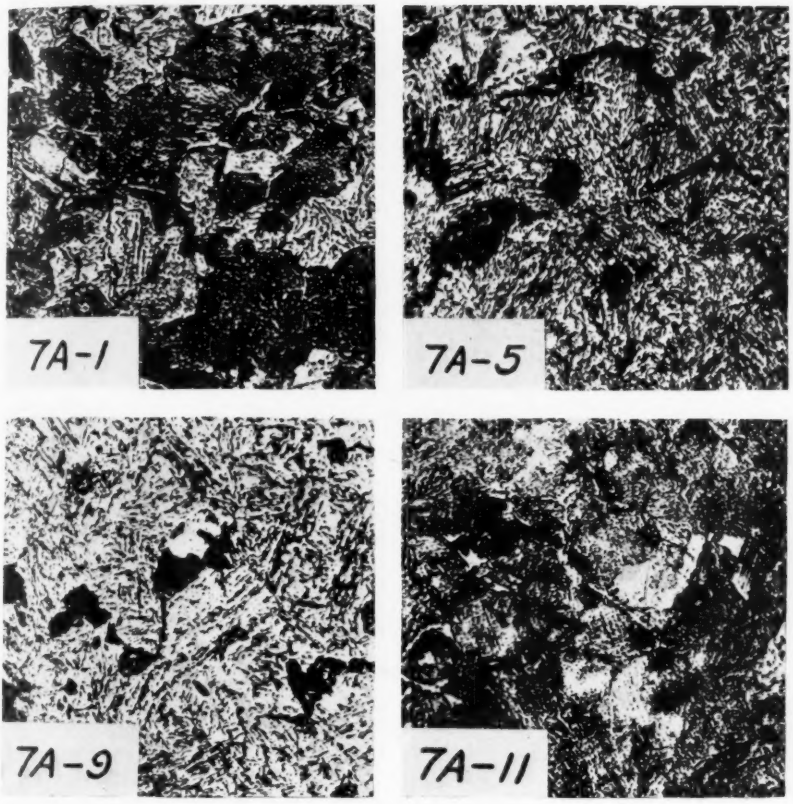

FIGURE 11.—*Microstructures and physical properties of some of the tensile specimens tested, summarized in Table 5*

Microstructures which were taken at center of the tensile specimens × 400; samples etched in 2 per cent HNO_3 in alcohol.

Specimen 7A–1, quenched in No. 2 oil at 20° C. (3 feet per second); tensile strength, 128,500 lbs./in.^{2}; elongation in 2 inches, 1.5 per cent; reduction of area, 4.7 per cent; Rockwell hardness, "C" scale, 31.

Specimen 7A–5, quenched in 5 per cent NaCl at 80° C. (3 feet per second); tensile strength 119,200 lbs./in.^{2}; elongation in 2 inches, 17.0 per cent; reduction of area, 47.2 per cent; Rockwell hardness, "C" scale, 49.

Specimen 7A–9, quenched in 5 per cent NaOH at 85° C. (3 feet per second); tensile strength, 77,500 lbs./in.^{2}; elongation in 2 inches, 1.0 per cent, reduction of area, 4.0 per cent; Rockwell hardness, "C" scale, 53.

Specimen 7A–11, quenched in 5 per cent NaOH at 90° C. (3 feet per second); tensile strength 114,700 lbs./in.^{2}; elongation in 2 inches, 20.5 per cent; reduction of area, 55.3 per cent; Rockwell hardness, "C" scale, 25.

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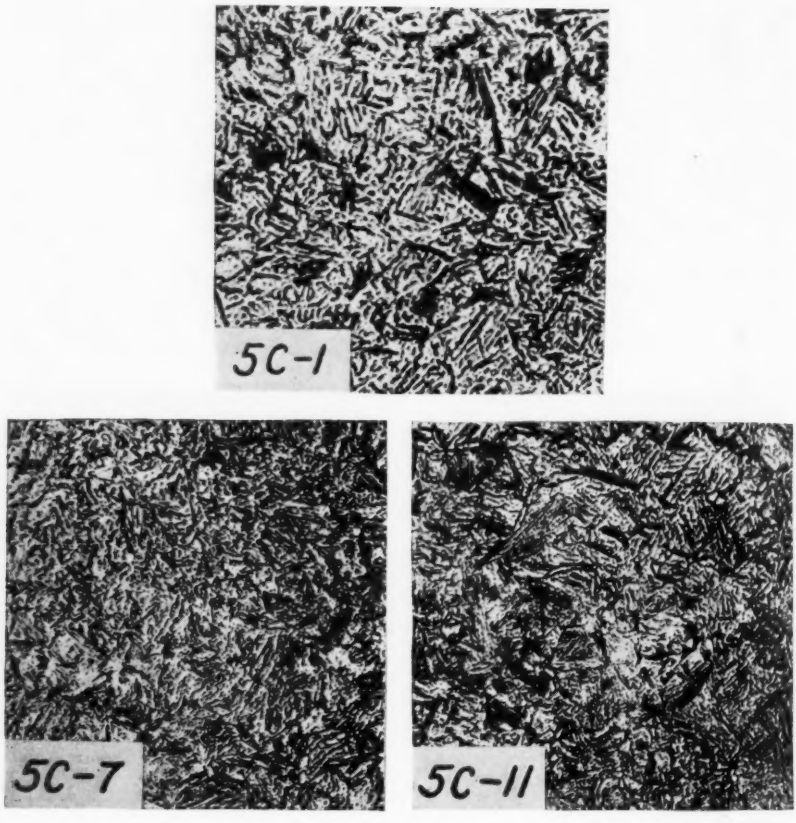

FIGURE 12.—*Microstructuers and physical properties of some of the tensile specimens tested, summarized in Table 4*

Microstructures which were taken at center of the tensile specimens × 400; samples etched in 2 per cent HNO_3 in alcohol.

Specimen 5C–1, quenched in No. 2 oil at 20° C. (3 feet per second); tensile strength, 225,600 lbs./in.^{2}; elongation in 2 inches, 12.5 per cent; reduction of area, 47.2 per cent; Rockwell hardness, "C" scale, 46.

Specimen 5C–7, quenched in 5 per cent NaOH at 80° C. (3 feet per second); tensile strength, 236,000 lbs./in.^{2}; elongation in 2 inches, 13.0 per cent; reduction of area 51.1 per cent; Rockwell hardness, "C" scale, 48.

Specimen 5C–11, quenched in 5 per cent NaOH at 90° C. (3 feet per second); tensile strength, 200,700 lbs./in.^{2}; elongation in 2 inches, 7.5 per cent; reduction of area, 20.0 per cent; Rockwell hardness, "C" scale, 46.

tempering of the martensite, to differences in the proportions of troostite present and to differences in the residual stresses left by the volume changes in hardening.

The three nickel-chromium steel samples shown in Figure 12 showed structures consisting of partially tempered martensite; in the sample quenched in 5 per cent sodium hydroxide at 90° C. dark needles were found suggesting the presence of troostite. These samples showed low tensile strength and ductility in comparison with the samples quenched in oil at 20° C. or 5 per cent sodium hydroxide at 80° C.

5. DIMENSIONAL CHANGES IN THE HOT AQUEOUS SOLUTIONS

Gages of the form and dimensions shown in Figure 13 were quenched in each of the two oils and in some of the hot aqueous solutions and

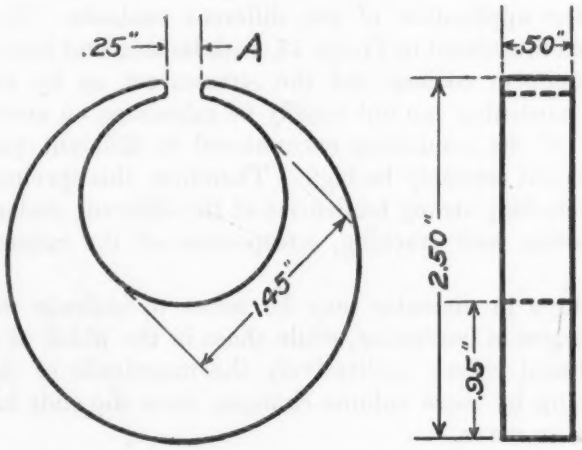

FIGURE 13.—*Form and dimensions of the gage used in the repeated quenching experiments*

the resulting changes in diameter and in the width of the slot *A* are summarized in Table 6.

The gages used were similar to those employed in the inspection of class 5 tool steels by the United States Navy Department,[13] except that they were exactly half size in all dimensions. Johanssen gage blocks were used in measuring the width of the slot *A* while the diameters were measured at points one-fourth to one-half inch from each side of the slot *A*. The gages were all brought to a constant temperature of 20° C. before measurements were made.

For the first quench the gages were placed in a furnace at 815° C., held 45 minutes and immersed in the chosen liquid. After the desired measurements had been made the gages were tempered for one hour at 230° C. and again measured. Subsequently, the gages

[13] 0.80 to 1.05 per cent C, 1.25 to 2.00 per cent Mn, Navy Department specifications for tool steel, No. 4785c; July 1, 1921.

were repeatedly quenched into the solutions first used, but in these cases they were held in the furnace only 15 minutes before quenching.

The steel originally selected for the tests was an "oil-hardening" steel containing about 0.9 per cent carbon, 1.2 per cent manganese, and about 0.5 per cent each of chromium and tungsten, but due to an error which was not discovered until after the experiments had been completed the gages were made from a steel containing 0.45 per cent carbon and 1 per cent chromium. However, this latter steel served the purpose of the experiments, since the coolants of greatest interest were those having cooling rates between the oils and ordinary tap water at atmospheric temperatures and an "oil-hardening" steel was not essential.

The object of the tests described was to detect in a practical and empirical manner conditions which might be characterized as dangerous in the application of the different coolants. The form of the specimen illustrated in Figure 13, with its thin and heavy sections, precludes uniform cooling and the stresses set up by the volume changes in hardening can not readily be calculated on account of the complexity of the conditions encountered in different parts of the gage but should certainly be high. Therefore, this specimen offers a means of detecting strong tendencies of the different coolants to promote distortion and cracking, irrespective of the causes of these effects.

The changes in diameter may be taken to indicate roughly the volume changes in hardening, while those in the width of the slot *A* (fig. 13) should reflect qualitatively the magnitude of the internal stresses set up by these volume changes, since the ends forming the slot are free to move.

As is shown in Table 6, the changes in the width of the slot *A* (fig. 13) were larger, per unit of measured length, than those in the diameter of the gages, but the two sets of changes showed simultaneous increases or decreases when comparing the different coolants. With one exception the changes were larger in the hot aqueous solutions than in the oils (Table 6). This one exception was the sodium hydroxide at 80° C., in which the dimensional changes were about equal to those in the No. 2 oil and smaller than the changes in any of the other liquids except the No. 1 oil. The Rockwell hardness produced in metal adjacent to the slot was somewhat higher when the gages were quenched in the sodium hydroxide at 80° C. (55, "C" scale) than when quenched in either of the oils (51 or 52 for both oils).

In all cases the changes produced by tempering for one hour at 230° C. were small, and this may be taken to indicate that the widening of the slot in quenching effectively relieved a large part of the internal stresses produced by the volume changes in hardening.

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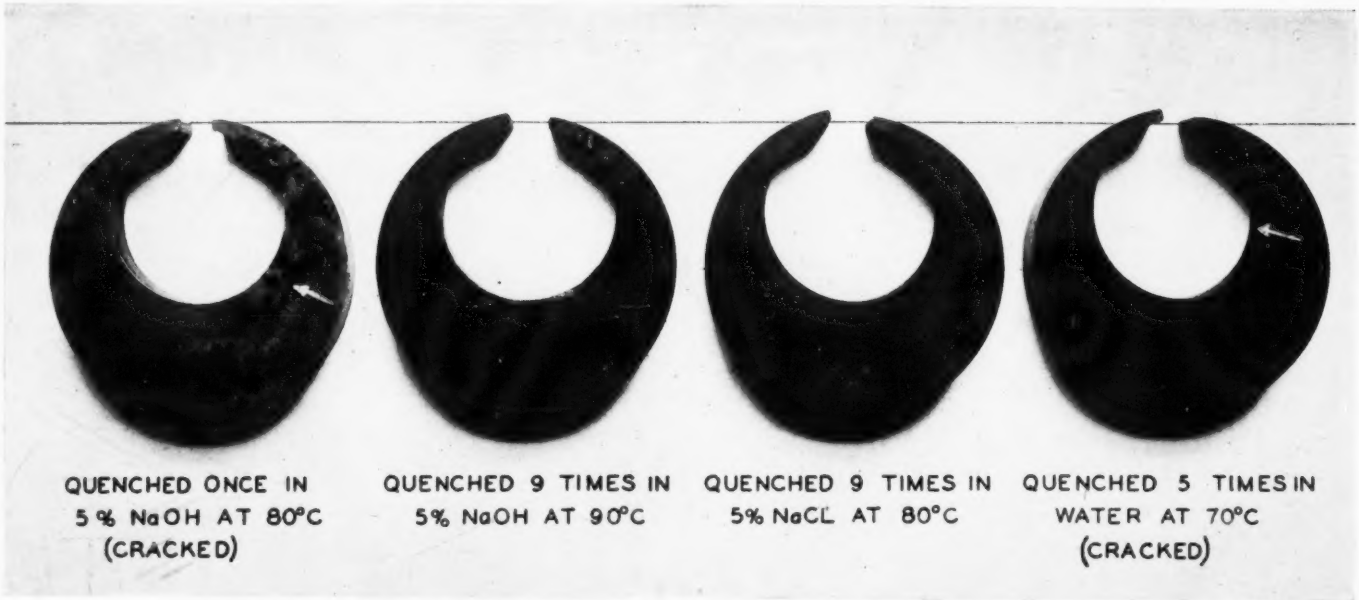

FIGURE 14.—*Some of the gages after repeated quenching in some of the hot aqueous solutions*

Arrows point to cracks.

The results obtained in these experiments justify the view that some of the hot aqueous solutions can be useful in bridging the gap between the cooling rates obtained with water and oils at ordinary temperatures, but some of their characteristics must be recognized as sources of danger or disadvantage. The maintenance of rapid cooling at low temperatures may be undesirable in the hardening of some steels, but this also applies to drastic coolants, such as the cold brines and cold sodium-hydroxide solutions, now used industrially. Difficulties from this source can be minimized in some cases, at least, by removing the steel before it reaches coolant temperatures (interrupted quenching) and under suitably controlled conditions any benefits derived need not be at the expense of high hardness. Another source of danger in the hot aqueous solutions is lack of uniformity, promoted by the formation of relatively large amounts of steam, but this becomes more marked as the bath temperature approaches the boiling point of water and can probably be counteracted through adequate circulation and adjustment of coolant composition and temperature.

Such sources of danger are well recognized, but the hot aqueous solutions studied are not necessarily "poisonous" to steels as is illustrated by the results of the repeated quenching summarized in Table 6.

Under the adverse conditions imposed by repeated introduction of the hardened steels into a furnace at high temperatures, without intermediate annealing, two of the gages cracked in the first and third quenchings in the 5 per cent sodium hydroxide at 80° C., but five treatments were required for cracking in water at 70° C., and the gages did not crack when quenched nine times in either 5 per cent sodium chloride at 80° C. or 5 per cent sodium hydroxide at 90° C.

The appearance of some of the repeatedly quenched gages is shown in Figure 14, and it will be observed that considerable distortion has taken place in the ends forming the slot in those gages which were quenched nine times without cracking. The cracks in the gages quenched in 5 per cent sodium hydroxide at 80° C. were in the heavy section (see arrows, fig. 14), whereas those in the gages quenched in water at 70° C. were circumferential at the hole in the specimen (see arrows, fig. 14).

Not enough tests have been made to determine the best of the liquids tested for different purposes nor the order of uniformity which may be expected under conditions of practical application, but the described results seem to justify the conclusion that the hot aqueous solutions will, upon further study of concentrations and circulation, offer a useful set of coolants to bridge the gap between water and oils at atmospheric temperatures, at least for the hardening of small steel parts.

TABLE 6.—*Dimensional changes and cracking of the gages shown in Figure 13 when repeatedly cooled in different liquids*

Coolant (moving at 3 ft./sec.)	Dimension A (fig. 13) in annealed steel	Change in A (fig. 13) upon quenching from 815° C.		Further change in A (fig. 13) upon tempering at 230° C.		Diameter change on quenching from 815° C.		Rockwell hardness ("C" scale)		Repeated quenching from 815° C. into specified coolant
		Individual specimens	Average	Individual specimens	Average	Individual specimens	Average	After first quench	After first quench and tempering at 220° C.	
	Inch	*Inch*	*Inch*	*Inch*	*Inch*	*Inch*	*Inch*			
No. 2 oil at 20° C	0.2482 .2482	+0.0037 +.0021	+0.0029	+0.0004 +.0003	+0.0004	+0.0037 +.0027	+0.0032	51 52	50 50	
No. 1 oil at 20° C	.2484 .2483	−.0001 +.0010	+.0005	+.0005 +.0007	+.0006	+.0025 +.0027	+.0026	52 51	49 49	
Water at 70° C	.2483 .2485	+.0090 +.0125	+.0108	+.0006 +.0004	+.0005	+.0072 +.0072	+.0072	57 57	52 51	Cracked on fifth quench.
5 per cent NaCl at 80° C	.2485 .2482	+.0134 +.0153	+.0144	+.0008 +.0007	+.0008	+.0056 +.0056	+.0056	57 55	51 52	Not cracked on ninth quench.
5 per cent NaOH at 80° C	.2477 .2483	+.0026 (1)	+.0026	+.0001	+.0001	+.0028	+.0028	55 56	51 51	Cracked on third quench. Cracked on first quench.
5 per cent NaOH at 90° C	.2484 .2485	+.0076 +.0084	+.0080	+.0005 +.0005	+.0005	+.0017 +.0021	+.0019	57 55	50 51	Not cracked on ninth quench.

[1] Cracked.

IV. SUMMARY

1. Surface and center cooling curves were obtained on cylinders of 0.96 per cent carbon steel, one-half inch in diameter and 2 inches long, when quenched from 875° C. into water, 5 per cent sodium hydroxide, 5 per cent sodium-chloride solutions, and two proprietary quenching oils at different temperatures between 20° and 100° C. The liquids were all moving at 3 feet per second and the cooling curves were correlated with the microstructures and the hardnesses produced in the cylinders.

2. Increase in temperature lowered the cooling speeds and increased the cooling times in water and the aqueous solutions, but the changes were smaller between 20° and 60° C. than between 60° and 100° C. Exactly opposite effects were produced in the center cooling by the two oils, but the changes were relatively small throughout the entire temperature range, 20° to 100° C.

3. As the temperature of the aqueous solutions approached the boiling point of water, the cooling at the surfaces of the cylinders became more irregular and the cooling rates at low temperatures around 200° or 300° C. became more rapid than at intermediate temperatures around 300° to 500° C. or at higher temperatures. However, smooth center cooling curves were obtained in water at temperatures up to and including 60° C. or the 5 per cent solutions of sodium hydroxide or sodium chloride up to 80° C.

4. These characteristics suggested the possibility of using the hot aqueous solutions to bridge the gap in cooling rates between water and the customary quenching oils at ordinary temperatures. The following were selected as the most promising of the liquids tested and are given in order of decrease in average cooling speeds (increase in center cooling times) over the range, 875° to 200° C.: 5 per cent NaOH at 20° C.; 5 per cent NaCl at 20° C.; water at 20° C.; 5 per cent NaOH at 60° C.; 5 per cent NaCl at 60° C.; water at 60° C.; 5 per cent NaOH at 80° C.; 5 per cent NaOH at 85° or 90° C.; the two proprietary oils at 20° to 100° C.

5. Not all of these would be classed as good coolants for practical heat treatment and substitutions or additions can be made from the group studied, but experimental application of some of the hot aqueous solutions in the quenching of medium carbon steel and nickel-chromium steel tensile test bars and a limited study of the dimensional changes and cracking of carbon-chromium steel gages of special form showed promising possibilities. The results seem to justify the view that the hot aqueous solutions should, with further study of concentrations and circulation, ultimately provide a useful set of coolants having speeds intermediate between water and oils at atmospheric temperatures, at least in the hardening of small pieces of steel.

V. ACKNOWLEDGMENTS

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RP104

PREPARATION OF EXPERIMENTAL SAGGER BODIES ACCORDING TO FUNDAMENTAL PROPERTIES

By R. A. Heindl and L. E. Mong

ABSTRACT

This report presents the results obtained in a preliminary study of sagger bodies and contains data on the modulus of elasticity, transverse breaking strength, plastic flow, thermal expansion, and resistance to failure due to heat shock of 55 sagger mixes representing 39 different bodies fired at either 1,230° or 1,270° C. The 16 bodies prepared in duplicate were tested both after firing at 1,230° and 1,270° C. The bodies were prepared from a total of 15 different clays of known properties, and each body was made from two clays and a mixture of graded grog. The grog was graded into sizes so as to result in two types of bodies, those having (1) a coarse and open-grained structure and (2) a dense and fine-grained structure. The data on the fired bodies show that those containing the fine sizes of grog have the higher modulus of elasticity, transverse strength, and in the majority of cases, thermal expansion. Very little difference in total porosity of the two types of bodies is indicated although the rate of absorption shows great differences. The data obtained in this preliminary study indicate that those bodies having a porosity of less than 25 per cent, a low modulus of elasticity, as high transverse strength as is compatible with the low modulus of elasticity, and low thermal expansion below 250° C. are the most desirable for sagger purposes.

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I. INTRODUCTION

The investigation of the properties of sagger clays and sagger bodies is a study which readily resolves itself into a number of phases, each of which is more or less complete in itself. Results obtained in the study at the Bureau of Standards of several of these individual phases have been previously reported.[1] The present paper describes recent studies which included the preparation of sagger bodies based on fundamental data, the making of small experimental saggers, and the determination of certain physical properties of the fired saggers and sagger bodies. It contains the results of tests made on 39 different sagger bodies prepared in the laboratory and on eight sagger bodies furnished by pottery manufacturers as well as on saggers made from all these bodies.

II. GENERAL

A study of the sagger body compositions used by 40 pottery and tile manufacturers shows a large variation in the number and percentages of different clays used and percentage and sizing of grog. It also shows that the "rule-of-thumb" practice is largely followed in the compounding of sagger bodies. The number of clays used in any one body varies from two to four, and the amount of grog in the various bodies ranges from approximately 30 to 60 per cent. The majority of sagger mixes fail to show any definite sizing or grading of grog. In some cases the grog is simply crushed to pass a sieve with fairly large openings, while in others only the coarse grog is used. In general, the raw clay content of most sagger mixtures consists of one or more dense firing or vitrifying clays and one or more open-burning and comparatively refractory clays, with varying percentages and sizes of grog.

The possible variations in clay combinations, sizing, percentage, and porosity of grogs and firing temperatures is practically unlimited with the many sagger clays on the market. It was, therefore, necessary to limit this study to the making and testing of such body compositions from the 17 representative clays as might result in data of most value for preparing saggers of maximum life.

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[1] I. Progress Report on Investigation of Sagger Clays, J. Am. Ceram. Soc., **9** (3), pp. 131-143; 1926. II. Progress Report on Investigation of Sagger Clays—Some Observations as to the Significance of Their Thermal Expansion, J. Am. Ceram. Soc., **9** (9), pp. 554-574; 1926. III. Progress Report on Investigation of Sagger Clays—Their Elasticity and Transverse Strength at Several Temperatures, J. Am. Ceram. Soc., **10** (7), pp. 524-534; 1927. IV. Progress Report on Investigation of Sagger Clays—Their Elasticity, Transverse Strength, and Plastic Flow at 1,000° C., J. Am. Ceram. Soc., **10** (12), pp. 995-1004; 1927.

III. SAGGER BODY COMPOSITIONS

The initial study of the compounding of sagger bodies included the blending of two clays, in equal parts by weights, mixed with equal proportions by weight of grog prepared from each clay. One of the clays when fired had a high porosity (open-burning) and the other a somewhat lower porosity (close-burning). The grogs used in these mixes were fired at approximately 1,230° C. (cone 9–9½) for one and one-half hours. This procedure was varied in several instances by using separately grog prepared from only one of the clays; that is, either the open-burning or the dense-burning clay. With one exception, only clays having the same general type of thermal expansion below 200° C. were used in a body; that is, each of the clays making up a body was taken from either group H or group L.[2] The sagger body numbers, the clays and grogs making up the various bodies, and the properties of these clays fired at 1,230° C. are given in Table 1.

The majority of the bodies were prepared in two series as similar as possible in every respect with the exception of the sizes of the grog. One series compounded with comparatively coarse sizes of graded grog was designated as "C" and the other series compounded with the finer sizes of graded grog was designated as "F." Two combinations of grog sizes were taken from those recommended by Kirkpatrick.[3] The one, consisting of the relatively coarser sizes of grog, is recommended where resistance to repeated heating and cooling is desired more than strength. In the other, finer sizes are used and resistance to repeated thermal shock is sacrificed to obtain bodies of greater strength.

In the two primary combinations used, the grog sizing and the percentage of each size are as follows:

Material	Sieve No.		Percentage of each size
	Passed—	Retained on—	
For coarse grogged body	4	8	20
	8	12	60
	12	20	20
For fine grogged body	20	40	66⅔
	40	80	33⅓

[2] Report II (footnote 1) states that the clays have been classed in two groups according to thermal expansion behavior between 100° and 200° C.; clays classed in Group L showed a decided increase in the rate of expansion, while clays of Group H showed a very small, or, in the majority of cases, no increase in rate of expansion.

[3] B. S. Tech. Paper No. 104, p. 38, Table 11.

TABLE 1.—*Data on clays* [1] *fired at 1,230° C. used in sagger bodies*

Sagger body Nos.	Numbers of clays in sagger bodies	Grog No.	Belong to group [2]	Porosity	Tested at 20° C. Modulus of— Rupture	Tested at 20° C. Modulus of— Elasticity	Saggers made from single clays cracked at—
				Per cent	*Lbs./in.²*	*1,000 lbs./in.²*	*° C.*
1F, 1C, 1aF, 1aC	24	24	H	29	2,180	2,770	570
	37	37	H	3	3,920	9,430	480
2F, 2C, 2aF, 2aC	24	24	H	29	2,180	2,770	570
	32	32	H	13	2,310	5,610	515
3F, 3C, 3aF, 3aC	19	19	H	34	1,380	1,530	800
	32	32	H	13	2,310	5,610	515
4F, 4C, 4aF, 4aC, 21SF, 4XF, 4XC	19	19	H	34	1,380	1,530	800
	24	24	H	29	2,180	2,770	570
5F, 5C, 5aF, 5aC, 1XF, 1XC	5	5	L	22	3,140	4,910	370
	41	41	L	36	2,350	3,110	350
6F, 6C, 6aF, 6aC, 20SF, 2XF, 2XC	6	6	L	32	600	889	410
	25	25	L	34	2,450	3,570	495
7F, 7C, 7aF, 7aC, 3XF, 3XC	15	15	H	15	3,305	5,210	580
	42	42	H	24	1,460	2,230	745
15S, 8F, 8C, 8aF, 8aC	5	5	L	22	3,140	4,910	370
	16	16	L	42	635	934	1,000
9F, 9C	15	15	H	15	3,305	5,210	580
	42	------	H	24	1,460	2,230	745
10F, 10C	6	6	L	32	600	889	410
	5	------	L	22	3,140	4,910	370
11F, 11C	41	41	L	36	2,350	3,110	350
	35	35	H	14	3,360	3,360	575
12F, 12C	24	39	H	29	2,180	2,770	570
	39	------	H	19	3,370	5,090	565
13F, 13C	18	49	L	17	3,010	5,950	405
	49	------	L	37	1,710	2,370	460
14F, 14C	18	18	L	17	3,010	5,950	405
	49	49	L	37	1,710	2,370	460

[1] Complete chemical and physical properties of these clays have been given in the four progress reports already published on this investigation. (See footnote 1 of text.)

[2] The second progress report (see footnote 1 of text) classed the clays according to rate of thermal expansion below 200° C. into Groups H and L.

The following special combinations of grog were used in one body each ("S" bodies):

1. Body 15S. Grog and dust passing an 80-mesh sieve.

2. Body 21S. F. Grog graded as follows to obtain a dense and strong body:

Sieve No.		Percentage used
Passed—	Retained on—	
20	40	40
40	80	20
80	200	40

3. Body 20S. F. Grog approximately graded in accordance with W. F. Fuller's curve [4] to obtain a body especially resistant to thermal shock and also of good strength.

Sieve No.		Percentage of each size
Passed—	Retained on—	
4	8	20
8	12	15
12	20	20
20	40	15
40	80	15
80	200	15

In addition, eight bodies were prepared, four each using the coarse and fine grog combinations, except that the grog was fired for one and one-half hours at 770° ± 5° C., instead of 1,230° C. These bodies ("X" bodies) were so prepared because it has been found that fire clays show a rapid contraction at about 800° C.[5] It was assumed that it might be desirable to use grog which has not been fired higher than this temperature so as to eliminate the strains which are likely to be set up between the bond and grog during firing if the latter had been first fired at a temperature considerably higher than 800° C.

IV. DESCRIPTION OF SPECIMENS

The grog used in the preparation of specimen bars and saggers had been fired in all cases to approximately 1,230° C. (cone 9½). Six bars 1 by 1 by 12 inches were prepared for the determination of modulus of elasticity and transverse strength. Specimens measuring approximately 1 by 1 by 6 inches were used for linear thermal expansion studies. These specimens were cut to size from the ruptured 1 by 1 by 12 inch bars used for modulus of elasticity determinations. Six specimens 1 by 1 by 7 inches were made for dry breaking-strength tests and five (in some cases six) saggers, 4 by 4 by 6 by ½ inches, were made for the thermal-shock test. The saggers were made oval in shape to more nearly simulate the conditions producing strains developed in saggers used in practice. One set of saggers and the 12-inch bars were fired at approximately 1,230° C. (cones 9–9½) and another set of each at 1,270° C. (cones 11½–12). To simulate industrial conditions which might cause some difference in the properties of the burned bodies, the saggers of any one set were not all made on the same day but on different days. All saggers were fired in the same kiln, a part of each set of five saggers being fired at different times.

[4] Concrete Plain and Reinforced, 1916 ed., by Taylor and Thompson.
[5] The Behavior of Fire Clays, Bauxites, etc., on Heating, Trans. Eng. Cer. Soc., **22**, p. 111; 1922–23.

V. METHODS OF TESTING AND RESULTS

The methods of determining the modulus of rupture, porosity, linear thermal expansion, resistance to thermal shock, modulus of elasticity, and transverse strength at room and elevated temperatures, and the plastic flow at 1,000° C., have been described in detail in the several previous reports.[6] It might be well, however, again to give briefly the method used in the quenching test. Five specimen saggers of each of the bodies were heated at progressively higher temperatures and air quenched until fracture occurred. The initial quenching was from 350° C., the second 400° C., and for each succeeding quenching the temperature was increased 25° C. until the test sagger failed.

1. MODULUS OF RUPTURE, UNFIRED BODIES

The moduli of rupture of the various sagger bodies, both those prepared in the laboratory and those received from the potteries, are given in Tables 2 and 3.

The average modulus of rupture for the bodies containing the fine grog was found to be 160 lbs./in.^{2}, for the bodies containing the coarse grog 95 lbs./in.^{2}, and for the commercial bodies 75 lbs./in.^{2}.

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[6] See footnote 1, p. 420.

TABLE 2.—*Properties of sagger bodies fired at 1,230° C.*

Body No.	Numbers of clays in body [1]	Modulus of rupture of unfired body	Tested at 20° C.			Tested at temperature at which sagger failed in quenching test				Tested at 750° C.			Porosity	Coefficient of expansion 20° to 250° C.	Coefficient of expansion 20° to 600° C.	Total expansion in per cent of unit length	Resistance factor "R"
			Modulus of—		Computed outer fiber strain	Sagger failing at—	Modulus of—		Computed outer fiber strain	Modulus of—		Computed outer fiber strain					
			Rupture	Elasticity			Rupture	Elasticity		Rupture	Elasticity						
		Lbs./in.²	*Lbs./in.²*	*1,000 lbs./in.²*	*Per cent*	*°C.*	*Lbs./in.²*	*1,000 lbs./in.²*	*Per cent*	*Lbs./in.²*	*1,000 lbs./in.²*	*Per cent*	*Per cent*	*×10⁻⁶*	*×10⁻⁶*	*20° to 1,000° C.*	
1F	24, 37	90	2,110	4,805	0.04	640	2,000	5,515	0.04	1,730	5,970	0.03	17.3	5.2	5.9	0.52	4.3
1C	24, 37	50	955	1,775	.05	835	885	1,465	.06	1,090	2,270	.05	17.6	4.7	5.6	.51	5.5
2F	24, 32	195	1,905	3,605	.05	560	2,205	4,630	.05	2,260	4,730	.05	19.9	6.7	6.4	.55	4.3
2C	24, 32	75	960	1,525	.06	680	985	2,605	.04	830	2,890	.03	23.8	6.6	6.4	.54	4.2
3F	19, 32	105	1,345	1,990	.07	760	1,940	3,500	.06	1,780	4,150	.04	24.6	5.5	6.2	.51	4.7
3C	19, 32	70	745	1,405	.05	860	850	1,530	.06	1,140	2,640	.04	24.3	5.5	6.0	.50	4.0
4F	19, 24	75	1,095	1,595	.07	640	1,610	2,690	.06	1,700	2,830	.06	33.4	7.5	7.2	.56	2.9
4C	19, 24	70	620	890	.07	645	910	1,580	.06	1,090	1,875	.06	34.2	7.6	7.6	.58	2.8
5F	5, 41	205	1,505	2,490	.06	445	1,970	3,520	.06	1,820	3,880	.05	28.4	8.9	7.3	.60	3.0
5C	5, 41	110	645	1,545	.04	585	805	2,260	.04	820	2,350	.04	28.4	8.5	7.0	.58	2.1
6F	6, 25	185	1,150	1,700	.07	550	1,620	2,850	.06	2,105	3,370	.06	31.6	10.0	8.3	.62	2.7
6C	6, 25	150	560	1,075	.05	610	920	1,960	.05	920	2,810	.03	30.0	9.3	8.0	.59	2.2
7F	15, 42	185	1,875	3,755	.05	610	1,910	5,330	.04	2,300	6,060	.04	19.2	4.5	5.4	.49	4.8
7C	15, 42	160	1,330	3,330	.04	690	1,355	3,330	.04	1,200	4,355	.03	16.6	4.3	5.4	.49	4.5
8F	5, 16	135	1,315	2,220	.06	450	1,570	2,650	.06	1,660	2,670	.06	35.5	8.9	6.9	.58	2.9
8C	5, 16	75	510	1,000	.05	500	720	1,270	.06	755	1,210	.06	34.9	7.8	6.5	.55	2.5
9F	15, 42	165	2,025	4,700	.04	565	2,020	5,280	.04	2,320	6,020	.04	17.3	4.7	5.7	.50	4.5
9C	15, 42	105	1,175	3,160	.04	650	1,340	4,285	.03	1,275	4,000	.03	18.2	4.3	5.4	.50	3.8
10F	6, 5	180	1,460	2,090	.07	440	1,880	2,530	.07	2,600	4,110	.06	30.4	10.0	8.6	.60	2.7
10C	6, 5	85	425	540	.08	600	750	1,350	.06	1,160	1,815	.06	33.0	9.1	9.1	.63	2.6
11F	41, 35	250	1,525	2,495	.06	565	1,675	3,505	.05	2,200	4,000	.05	24.5	7.0	6.2	.53	4.0
11C	41, 35	120	660	1,340	.04	715	770	2,280	.03	930	2,460	.04	24.0	6.6	6.1	.52	3.5
12F	24, 39	120	1,980	3,680	.05	535	1,865	3,030	.06	2,180	4,110	.05	25.7	6.1	6.2	.53	3.5
12C	24, 39	80	940	2,280	.04	615	1,200	3,140	.04	1,090	3,340	.03	24.2	5.9	5.9	.51	2.6
13F	18, 49	130	1,510	2,020	.07	585	1,550	2,805	.06	1,370	3,220	.04	35.1	6.7	6.0	.51	3.6
13C	18, 49	95	690	1,390	.05	725	1,155	2,555	.05	1,050	1,825	.06	31.9	6.4	6.0	.51	2.7
14F	18, 49	125	1,510	2,625	.06	535	1,490	3,320	.05	1,900	3,530	.05	28.1	6.9	6.4	.54	3.3
14C	18, 49	85	770	1,400	.06	610	1,130	2,425	.05	950	2,520	.04	26.7	6.8	6 1	.53	3.4
15S	16, 5	180	2,685	3,625	.07	350	2,790	4,300	.06	2,460	4,670	.05	28.8	9.8	7.5	.58	3.0
1XF	5, 41	170	3,250	5,335	.06	465		5,750	.05	3,670	7,010	.05	19.4				
1XC	5, 41	65	1,350	2,380	.06	585	1,245	2,960	.04	1,400	3,410	.04	20.9				
2XF	6, 25	180	2,240	3,255	.07	445	1,510	3,620	.07	2,540	3,980	.06	29.6				
2XC	6, 25	75	910	1,645	.06	590	1,530	2,960	.05	1,360	3,930	.03	29.0				
3XF	15, 42	260	3,985	7,185	.06	465	3,660	7,510	.05	3,700	9,165	.04	7.6				
3XC	15, 42	145	1,825	3,940	.05	590	1,855	5,890	.03	1,800	6,025	.03	12.0				
4XF	19, 24	95	1,585	2,110	.07	625	1,890	4,070	.05	2,400	4,400	.05	31.4	5.5	6.7	.53	3.5
4XC	19, 24	80	1,215	1,740	.07	665	1,490	2,900	.05	1,780	3,300	.05	30.4	4.8	6.5	.50	3.4

[1] Identification numbers of clays correspond to those used in previous reports published on this investigation.

TABLE 3.—*Properties of sagger bodies fired at 1,270° C.*

Body No.	Numbers of clays in body [1]	Modulus of rupture of unfired body	Tested at 20° C.			Tested at temperature at which sagger failed in quenching test				Tested at 750° C.			Tested at 1,000° C.				Porosity	Coefficient of expansion 20° to 250° C.	Coefficient of expansion 20° to 600° C.	Total expansion in per cent of unit length	Resistance factor "R"
			Modulus of—			Sagger failing at—	Modulus of—			Modulus of—			Modulus of—		Computed outer fiber strain using—						
			Rupture	Elasticity	Computed outer fiber strain		Rupture	Elasticity	Computed outer fiber strain	Rupture	Elasticity	Computed outer fiber strain	Rupture	Elasticity	Tangent modulus	Secant modulus					
		Lbs./in.²	*Lbs./in.²*	*1,000 lbs./in.²*	*Per cent*	*° C.*	*Lbs./in.²*	*1,000 lbs./in.²*	*Per cent*	*Lbs./in.²*	*1,000 lbs./in.²*	*Per cent*	*Lbs./in.²*	*1,000 lbs./in.²*	*Per cent*	*Per cent*	*Per cent*	*×10⁻⁶*	*×10⁻⁶*	*20° to 1,000° C*	
1aF	24, 37	(2)	2,280	5,980	0.04	580	2,430	7,210	0.03	2,790	------	0.05	4,130	740	0.56	0.69	18.1	(2)	(2)	(2)	3.7
1aC			1,195	3,280	.04	595	1,035	3,640	.03	1,300	3,810	.03	2,210	490	.45	.63	16.9	(2)	(2)	(2)	3.9
2aF	24, 32	(2)	2,180	4,205	.05	525	2,340	4,890	.05	2,350	5,750	.04	2,655	1,250	.21	.44	20.3	(2)	(2)	(2)	4.1
2aC			1,130	2,340	.05	565	1,370	3,540	.04	1,400	3,540	.04	1,610	770	.21	.44	21.7	(2)	(2)	(2)	3.6
3aF	19, 32	(2)	1,570	2,520	.06	630	2,560	5,140	.03	2,440	4,770	.05	3,070	1,015	.30	.46	23.6	(2)	(2)	(2)	4.2
3aC			1,200	1,960	.06	710	1,585	3,695	.04	1,740	3,650	.05	1,845	820	.23	.36	22.9	(2)	(2)	(2)	4.4
4aF	19, 24	(2)	1,250	1,730	.07	460	1,630	2,330	.07	1,980	3,180	.06	2,940	1,280	.23	.32	32.6	(2)	(2)	(2)	3.3
4aC			1,000	1,465	.07	490	1,080	1,650	.07	1,480	2,820	.05	1,980	920	.22	.28	32.1	(2)	(2)	(2)	3.1
5aF	5, 41	(2)	1,720	3,220	.05	400	1,660	3,950	.04	2,110	4,300	.05	3,500	830	.42	.62	26.9	(2)	(2)	(2)	2.6
5aC			965	1,900	.05	450	925	2,300	.04	935	2,440	.04	1,610	555	.29	.61	25.5	(2)	(2)	(2)	2.9
6aF	6, 25	(2)	1,500	1,960	.08	400	1,370	2,110	.07	1,970	3,290	.06	2,710	1,120	.24	.30	30.3	(2)	(2)	(2)	3.0
6aC			765	1,180	.07	490	1,030	1,770	.06	1,040	1,970	.05	1,550	785	.20	.51	31.0	(2)	(2)	(2)	2.7
7aF	15, 42	(2)	2,095	5,370	.04	550	3,400	6,520	.05	2,910	5,860	.05	4,650	470	.99	1.27	16.2	(2)	(2)	(2)	4.7
7aC			1,150	4,180	.03	565	1,740	4,410	.04	1,500	3,650	.04	775	230	.34	1.77	16.2	(2)	(2)	(2)	3.3
8aF	5, 16	(2)	1,590	2,240	.07	400	2,190	2,970	.07	1,760	2,910	.06	2,790	1,190	.23	.26	35.6	(2)	(2)	(2)	2.6
8aC			1,025	1,430	.07	450	1,210	2,065	.06	1,200	2,120	.06	1,325	785	.17	.26	34.3	(2)	(2)	(2)	3.2
20SF	6, 25	70	1,050	1,675	.06	460	1,285	2,150	.06	1,740	2,940	.06	2,080	1,105	.19	.25	30.7	8.9	8.1	.59	2.5
21SF	19, 24	55	1,485	1,860	.08	455	1,830	2,310	.08	2,200	3,010	.07	3,840	1,085	.35	.38	33.3	7.4	7.4	.56	3.4
COMMERCIAL BODIES																					
A	--------	110	1,215	2,890	0.04	470	1,350	3,180	0.04	1,630	3,880	0.04	1,920	940	0.20	0.29	26.3	8.5	7.2	0.57	2.2
B	--------	85	1,200	2,465	.05	485	1,380	2,940	.05	1,620	3,400	.05	2,350	1,360	.17	.24	27.1	8.8	7.0	.56	2.6
C	--------	90	945	1,620	.06	680	915	2,810	.03	1,150	2,010	.06	------	------	------	------	23.7	9.0	7.8	.57	3.3
D	--------	------	1,415	3,160	.04	415	1,960	4,820	.04	------	------	------	------	------	------	------	25.6	9.5	7.3	.59	2.3
E	--------	95	855	1,355	.06	615	1,110	2,480	.05	1,420	2,450	.06	1,580	730	.22	.58	29.9	8.2	7.0	.54	3.0
F	--------	55	660	1,730	.04	430	1,170	1,780	.07	1,360	2,850	.05	1,035	685	.15	.24	29.3	6.9	6.3	.52	2.2
G	--------	55	1,070	2,290	.05	440	1,055	2,630	.04	925	2,980	.02	1,780	735	.24	.50	27.9	8.6	6.9	.58	2.3
H	--------	40	750	1,150	.07	645	1,200	2,390	.05	------	------	------	1,130	405	.28	.65	26.6	7.1	6.3	.52	3.9

[1] Identification numbers of clays correspond to those used in previous reports published on this investigation.
[2] Values for bodies 1aF to 8aC, inclusive, were considered the same as those given in Table 2 for bodies 1F to 8C, respectively.

2. POROSITY

The porosities of the sagger bodies fired at 1,230° C. are given in Table 2 and those of the bodies fired at 1,270° C. are given in Table 3. The range in porosity, for the bodies fired at 1,230° C., is from approximately 8 to 35.5 per cent and for the bodies fired at 1,270° C. from 16 to 35.6 per cent. As shown earlier in this report, there is considerable difference in the sizes of the grog used in the preparation of coarse and fine grogged bodies. A macroscopic examination of the texture of the sagger bodies also shows a decided difference in structure of the fine and coarse grogged bodies. In practically all cases, very little difference in porosity was found for any pair of bodies of the same key number whether the grog was fine or coarse grained. Consequently, the relative pore size of the fine and coarse grogged sagger bodies was determined by measuring the rate of absorption of the bodies after complete immersion in water at room temperature for certain time intervals, namely 5 minutes, 1 hour, and 48 hours. The results given in Table 4 of the tests made on specimen bars, show great differences in porosity of bodies fired at 1,270° C.

TABLE 4.—*Rate of absorption (pore size) in terms of porosity (bodies fired at 1,270° C.)*

Body No.	Results obtained after immersing specimens—			Total porosity	Body No.	Results obtained after immersing specimens—			Total porosity
	5 minutes	1 hour	48 hours			5 minutes	1 hour	48 hours	
	Per ct.	*Per ct.*	*Per ct.*	*Per ct.*		*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*
1aF	3.83	6.55	7.60	16.1	6aF	17.25	24.32	25.90	31.9
1aC	9.53	9.64	10.45	17.6	6aC	22.30	22.95	26.76	31.7
2aF	2.84	5.60	9.56	18.8	7aF	2.43	4.82	7.15	15.2
2aC	12.60	12.50	15.65	18.5	7aC	8.75	8.72	9.55	15.7
3aF	7.55	14.75	16.85	24.8					
3aC	12.68	13.91	17.95	24.5	8aF	20.20	27.90	29.30	34.6
4aF	17.54	26.25	28.17	32.4	8aC	26.80	26.70	28.75	33.3
4aC	25.03	25.32	28.00	31.3	20SF	18.83	24.85	27.00	31.2
5aF	13.98	14.32	17.12	25.6	21SF	16.00	27.95	29.65	33.8
5aC	17.25	17.08	18.52	25.1					

3. LINEAR THERMAL EXPANSION

The average coefficient of linear expansion between 20° [7] and 250° C., 20° and 600° C., and also the total expansion at 1,000° C. in per cent of unit length are given in Table 2 for the specimens fired at 1,230° C., and in Table 3 for certain specimens fired at 1,270° C. The results obtained on the 30 bodies fired at 1,230° C. indicate that, when blending two clays and grog prepared from either one or both clays, the resulting expansion behavior of the mixture may fall into one of the three following classes:

1. It may be greater than the expansion of either clay contained in the body. In this group are included bodies Nos. 2F, 2C, 4F, 4C, 12F, and 12C.

[7] The average room temperature was approximately 20° C. during these experiments.

2. It may be approximately equal to the average expansion of the clays making up the body. This group contains bodies Nos. 3F, 3C, 4XF, 4XC, 6F, 6C, 10F, 10C, 11F, and 11C.

3. It may be approximately the same as that of the clay in the body having the lower expansion. Bodies Nos. 1F, 1C, 5F, 5C, 7F, 7C, 8F, 8C, 9F, 9C, 13F, 13C, 14F, and 14C are in this group.

An illustration of the expansion behavior of bodies grouped in class 1 is shown on the left in Figure 1. Full line curves represent the linear thermal expansion from 20° to 1,000° C. of each of the two clays used in the preparation of bodies Nos. 4F and 4C, and broken lines those obtained on these bodies. The curves for the bodies are practically identical in this instance. Since all the bodies in class 1 contain clay No. 24, it would appear that this clay when blended with another clay and the grog made from it produces no effect on the thermal expansion of the blend fired at 1,230° C. Although bodies 4XC and 4XF have an expansion behavior similar to those grouped in class 2, the expansion curves are shown in the left section of Figure 1 to facilitate comparison with the curves for bodies 4C and 4F. Bodies 4XF and 4XC are identical in every respect with bodies Nos. 4F and 4C, respectively, except that the grog used in the former had been fired to approximately 775° C. instead of 1,230° C. Due to the comparative softness of the grog fired at 775° C., it disintegrated somewhat during mixing with the clays and pugging of the body which caused a more intimate mixture of clays and grog than if the grog had been fired at a considerably higher temperature. This, together with the fact that the clay as grog had not altered as much in its physical properties when fired at 775° C. as when fired at 1,230° C., probably was the cause of a more complete reaction occurring between the constituents in the clay and grog which resulted in an expansion approximately the average of the two individual clays.

An example of the expansion of bodies grouped in class 2 is shown in the center section of Figure 1. The curves given were obtained on bodies 10F and 10C which were prepared from clays Nos. 5 and 6 and grog made from these clays. The expansion curves for the individual clays are also shown.

To the right in Figure 1 are given the expansion curves of bodies 14F and 14C, which are included in class 3. These bodies were made of clays Nos. 18 and 49, and grog from the same clays fired at 1,230° C. The thermal expansion curves for the individual clays, also given, show a large difference in total expansion. Since the expansions of the bodies closely approach the lower and more desirable expansion of clay No. 18, it would indicate that the selection of clays as far as this property is concerned was favorably made. Apparently most clays blended as in this study act favorably with respect

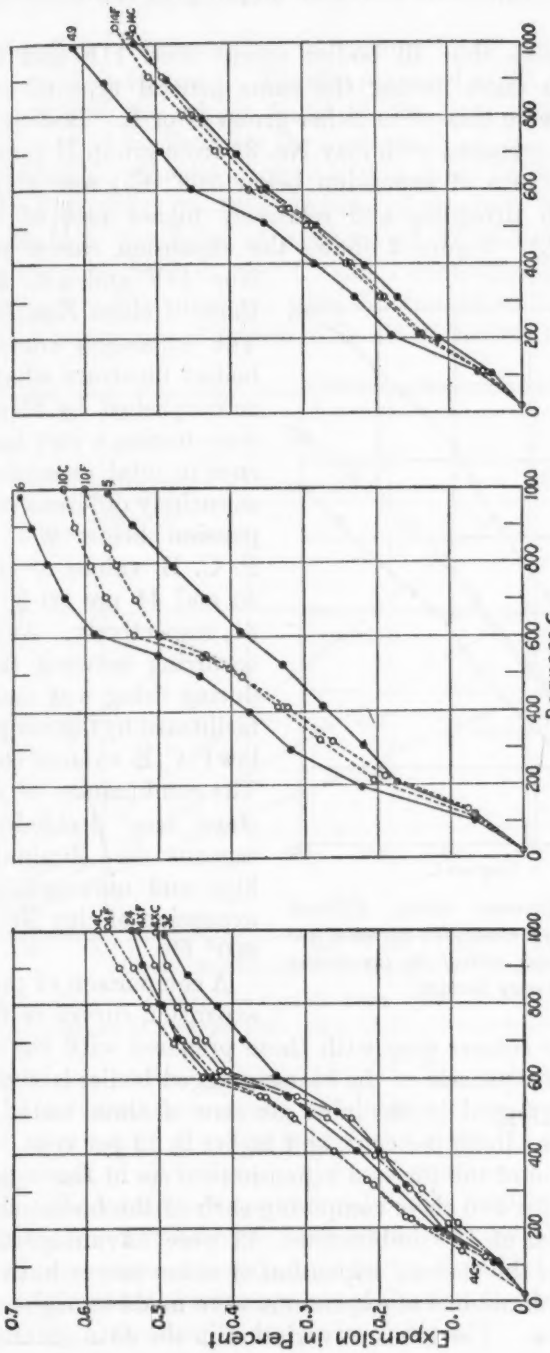

FIGURE 1.—*Thermal expansion curves of representative clays and of bodies prepared from them*

The curves illustrate the various changes which may occur in the thermal expansion when clays are blended

to the thermal expansion since the majority of bodies are classed in this group.

Table 1 shows that all bodies except Nos. 11F and 11C were prepared from clays having the same general type of expansion; that is, both were classed in either group H or L. Bodies Nos. 11F and 11C were prepared with clay No. 35 from group H (uniform and relatively low rate of expansion below 200° C.) and clay No. 41 from group L (irregular and relatively higher rate of expansion below 200° C.). Figure 2 shows the expansion curves for bodies Nos. 11F and 11C as well as those of clays Nos. 35 and 41. The expansion curves of the bodies illustrate what may be accomplished by blending two clays having a very large difference in total expansion as well as entirely different rates of expansion below 200° C. The P. C. E. values of clays Nos. 35 and 41 are 20–26 and 30–31, respectively. Any reaction occurring between these clays during firing was undoubtedly facilitated by the comparatively low P. C. E. value of clay No. 35. The combination of these two clays was decidedly advantageous in eliminating the high and unfavorable rate of expansion of clay No. 41 below 200° C.

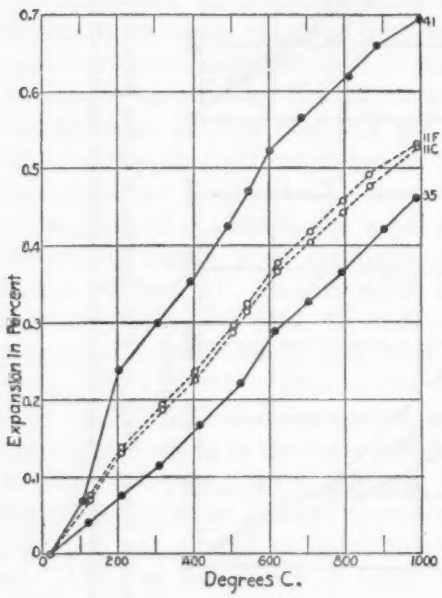

FIGURE 2.—*Showing widely different types of thermal expansion curves of two clays (full lines) and of the two bodies in which they were blended*

A comparison of the thermal expansion curves of the bodies containing the coarser grog with those prepared with the finer grog shows that the expansion of the coarse-grogged bodies is slightly lower than the fine-grogged bodies in 67 per cent of those tested, approximately the same in 20 per cent, and higher in 13 per cent.

A comparison of the thermal expansion curves of the sagger bodies with those of the two clays composing each of the bodies shows that out of the total of 15 combinations, 12 were advantageously made with respect to the thermal expansion of either one or both clays.

Check determinations of expansions were made on eight specimens of sagger bodies. The greatest variation in the data obtained on the same body was less than ± 2½ per cent.

4. MODULUS OF ELASTICITY AND TRANSVERSE STRENGTH

The deflections corresponding to various loads applied to body 20SF are plotted in Figure 3. Results obtained at 20, 460 (the temperature at which the sagger failed in the heat shock test), and 750° C. are plotted to illustrate the increase in resistance to bending of sagger bodies as the temperature within these limits is increased.

Bodies fired at 1,230° C.—The modulus of elasticity and transverse breaking strength (modulus of rupture) of 37 bodies, including 8 containing the grog fired at 775° C. and 1 containing grog and dust passing through a No. 80 sieve, were determined at room temperature, at the temperature of failure in an air-quenching test of saggers

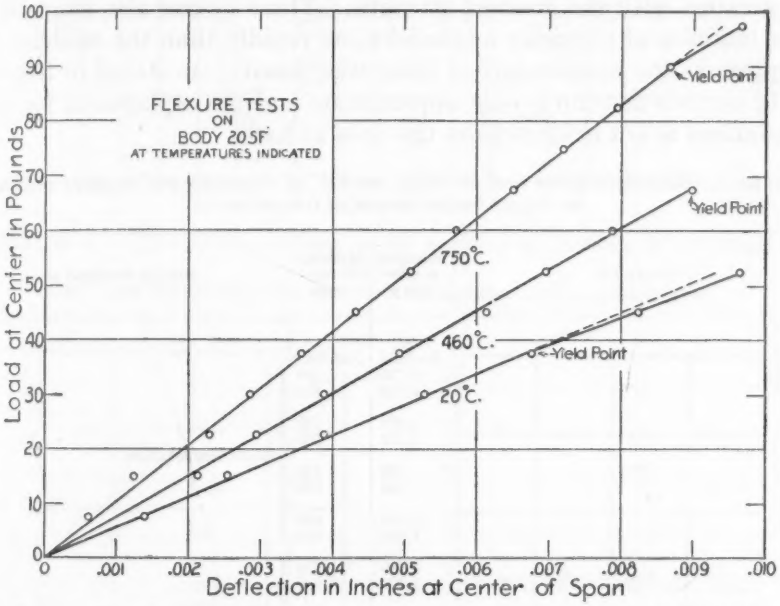

FIGURE 3.—*Curves showing the typical stress (load) strain (deformation) relation of a sagger body tested at three temperatures*

made from these bodies and at 750° C. The values obtained on 1 by 1 by 12 inch specimens, using a 10-inch span are given in Table 2.

Bodies fired at 1,270° C.—The modulus of elasticity and transverse breaking strength of 18 bodies, including 2 containing special graded grog sizes, and in addition 8 commercial bodies fired at 1,270° C. are given in Table 3. These bodies were tested at 1,000° C. in addition to the three temperatures specified for bodies fired at 1,230° C. The composition and order of arrangement of the first 16 bodies in Table 2 are identical with the first 16 bodies in Table 3.

The results indicate that there is a slight tendency for the bodies to show increased transverse breaking strength with increased tem-

peratures to 1,000° C., the maximum temperature used in these tests. The same holds true regarding the modulus of elasticity up to 750° C. At 1,000° C. the latter property shows a decided decrease. The percentage increase in the modulus of elasticity attending an increase in temperature from 20 to 750° C. is greater than the corresponding increase in cross-breaking strength. Figure 4 shows the effect of temperature on the modulus of elasticity of bodies fired at 1,270° C. The curves are presented in three sections to facilitate examination.

Values for the modulus of rupture determined at approximately 20° C. for bodies fired at 1,230° and 1,270° C. and plotted as in Figure 5 indicate that the ordinary or usual relation exists between transverse strength and modulus of elasticity; that is, the modulus of elasticity is greatest with the greatest strength. These figures also show that the modulus of elasticity increased more rapidly than the modulus of rupture as the temperature of firing was raised. As stated in Report III,[8] the relationship is only approximate and the explanation for the variations is not evident from the data at hand.

TABLE 5.—*Determinations and checks of moduli of elasticity and rupture obtained on sagger bodies at several temperatures*

Body No.	Modulus of elasticity	Modulus of rupture	Results obtained at—
	1,000 lbs./in.²	*Lbs./in.²*	
4XC	1,730	1,210	Room temperature.
	1,740	1,215	
8C	1,000	510	
	1,110	500	
10C	520	450	
	565	395	
11C	1,340	660	
	1,625	600	
3F	3,920	1,770	Temperature at which sagger failed in heat shock test.
	3,500	1,940	
5F	3,520	1,970	
	3,560	1,920	
6C	1,960	950	
	1,960	920	
7C	3,050	1,185	
	3,330	1,355	
9C	4,400	1,200	
	4,285	1,340	
9F	5,920	(a)	750° C.
	6,020	2,320	
13F	3,100	(a)	
	3,100	2,320	
6aC	1,180	765	Room temperature.
	1,200	760	
6aC	785	1,550	1,000° C.
	700	1,420	

[a] No data obtained.

[8] See footnote 1, p. 420.

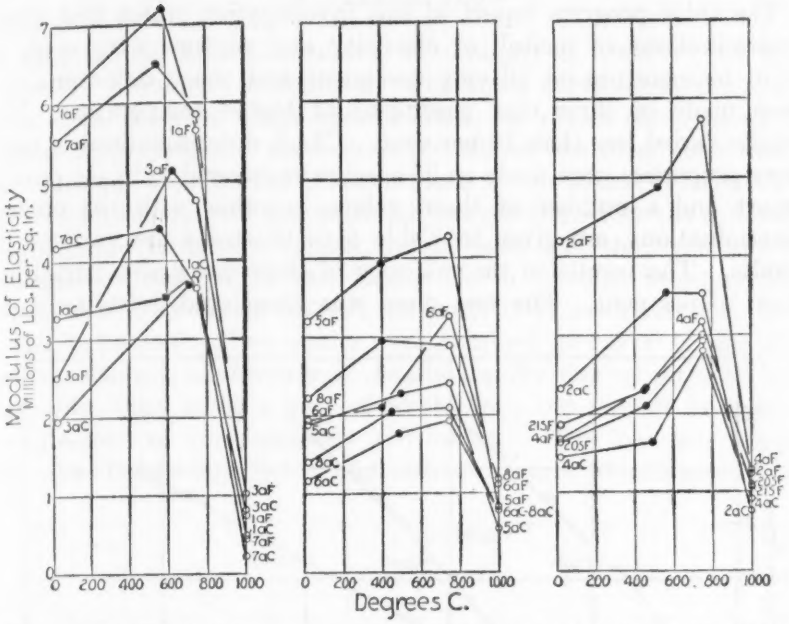

FIGURE 4.—*Effect of temperature on the modulus of elasticity of 18 sagger bodies*

Filled circles indicate temperatures at which saggers failed in the air-quenching test

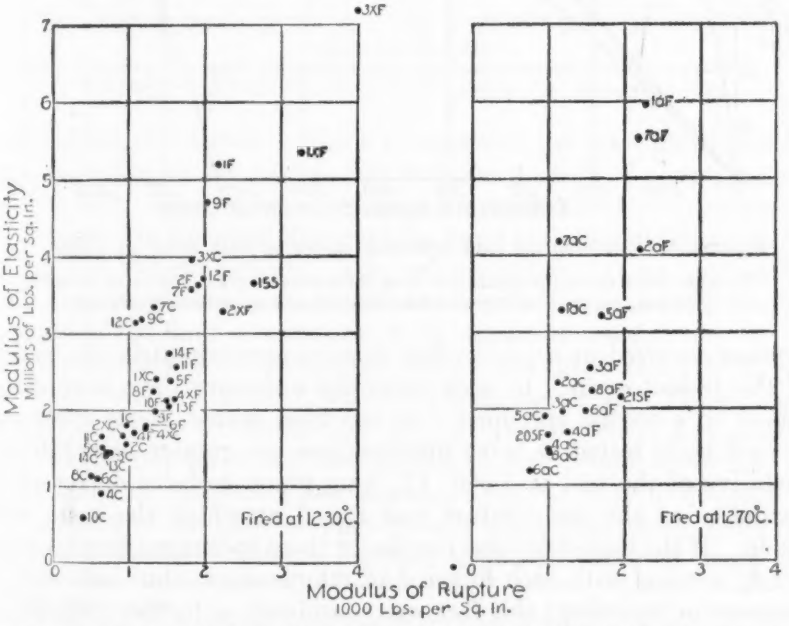

FIGURE 5.—*Showing the relation between modulus of elasticity and transverse strength (modulus of rupture) determined at room temperature of sagger bodies fired at either 1,230° or 1,270° C.*

The third progress report of this investigation states that check determinations of moduli of elasticity and rupture were made at room temperature on all clay specimens and check determinations were made of three clay specimens at higher temperature. The results varied less than 10 per cent. Check determinations of these same properties were made on 25 specimens referred to in the present report and a number of these values, together with the original determinations, are given in Table 5 to illustrate the variation in results. The results in the majority of these cases also varied less than 10 per cent. The test piece was considered defective if the

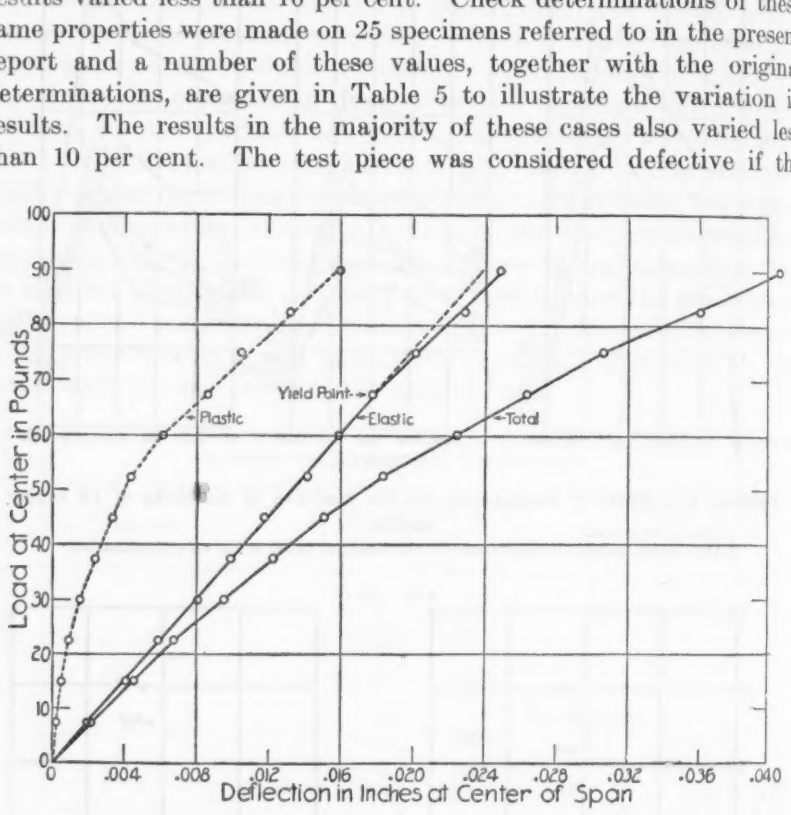

FIGURE 6.—*Showing the load-deflection curves of body 20SF at 1,000° C.*

The upper curve shows the plastic flow or set of the material, the middle curve the elastic deflection, and the lower curve the total deflection at each of the loads indicated

rupture occurred at a point other than at approximately the middle of the 10-inch span. In such cases the necessary data were determined on a second specimen. As has been stated, those specimens of each body tested at three temperatures not greater than 750° C., exclusive of the test at 1,000° C., were found to have decreased in flexibility as the temperature was raised at which the tests were made. If the load-deflection curves for these specimens became more nearly vertical with each increase of temperature (thus indicating a decrease in flexibility) this fact was considered as further evidence of the specimens being free from important defects.

5. PLASTIC FLOW

Typical load deflection curves, as obtained at 1,000° C. for body No. 20SF are shown in Figure 6. The upper curve shows the plastic flow of the material under various loads, the center curve shows the elastic properties, and the lower curve shows the total deflection of the specimen at each of the loads indicated. As stated in Report IV,[9] the elastic recovery of the material was considered as the difference between the deflection caused by the load and the "set" of the material on removal of this load. The deflections resulting from plastic flow of 24 sagger bodies fired at 1,270° C. are given in columns 2 and 3, Table 6. The results were obtained at 1,000° C. and they are the average of increments obtained every five minutes for one-half hour when using a load of 30 lbs./in.^{2}, and for one hour when using a load of approximately 120 lbs./in.^{2}. The load was applied midspan of the 1 by 1 by 12 inch specimens on a 10-inch span. The

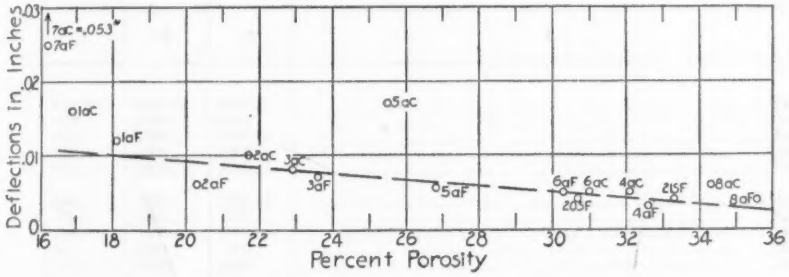

FIGURE 7.—*Effect of porosity on the plastic flow of sagger bodies*

values given in column 4, Table 6, represent the total plastic deflection, in inches, of the various bodies under a stress of approximately 240 lbs./in.^{2}. The values, taken from curves similar to that identified as "plastic" in Figure 6, illustrate the large variation in this property among the various bodies. It is quite possible that an appreciable error may be present in the results obtained with a load of 30 lbs./in.^{2} because of the limit of accuracy of the apparatus used.

For convenience the porosities of the bodies fired at 1,270° C. are shown in column 5, Table 6, with the plastic-flow data. These values plotted in Figure 7 indicate that, as illustrated by one of a number of lines which may be drawn through the plotted points, there may be a tendency for the plastic flow (column 4) of the body to decrease as the porosity of the body becomes greater when determined under the conditions stated.[10] Such a relation might be expected, since the

[9] See footnote 1, p. 420.

[10] This relationship would possibly become more exact if deflection determinations had been made on several specimens instead of only one, as in the present study. The porosity given is the average of five determinations.

fluxes introduced by the clays in a dense sagger body have a greater opportunity for reaction during firing than if present in a less dense body.

TABLE 6.—*Plastic flow data determined on sagger bodies fired at 1,270° C.*

Body No.	Average of deflection readings, in inches, taken at 5-minute intervals, on a 1 by 1 by 12 inch specimen, using a 10-inch span and temperature of 1,000° C.		Total plastic deflection, in inches (taken from plastic flow curves), at 1,000° C. with a stress approximately 240 lbs./in.²	Porosity
	During one-half hour, using stress approximately 30 lbs./in.²	During 1 hour, using stress approximately 120 lbs./in.²		
1	2	3	4	5
				Per cent
1aF	0.0002	0.0002	0.012	18.1
1aC	.0002	.0003	.016	16.9
2aF	<.0001	<.0001	.006	20.3
2aC	<.0001	.0001	.010	21.7
3aF	<.0001	<.0001	.007	23.6
3aC	<.0001	.0001	.008	22.9
4aF	<.0001	<.0001	.003	32.6
4aC	<.0001	<.0001	.005	32.1
5aF	.0001	.0002	.017	26.9
5aC	.0002	.0003	.017	25.5
6aF	.0001	.0001	.005	30.3
6aC	.0001	.0001	.005	31.0
7aF	.0002	.0004	.025	16.2
7aC	.0002	.0007	.053	16.2
8aF	<.0001	<.0001	.004	35.6
8aC	.0001	.0001	.006	34.3
208F	<.0001	<.0001	.004	30.7
218F	<.0001	.0001	.004	33.3
A	.0001	.0001	.012	26.3
B	.0001	.0001	.004	27.1
E	.0001	.0001	.011	29.9
F	.0001	.0001	.018	29.3
G	.0001	.0001	.016	29.9
H	.0001	.0002	.011	26.6

Bodies 7aF and 7aC, although showing good resistance in the heat-shock test, would undoubtedly prove unsatisfactory for sagger purposes because of a comparatively high plastic flow at 1,000° C.

6. AIR QUENCHING OR DUNTING TESTS

The results, showing the average temperature of failure of five small oval saggers in the heat-shock test, are given in Table 2 for the saggers fired at 1,230° C. and in Table 3 for the saggers fired at 1,270° C. Table 3 also contains the results of the tests on saggers prepared from commercial sagger bodies furnished by several potteries.

FIGURE 8.—*Saggers illustrating the three types of failures which occurred in the thermal shock test*

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The types of failure encountered during the testing of these saggers are shown in Figure 8. Sagger No. 1 illustrates a failure found only in saggers prepared from bodies containing the fine grog sizes. Sagger No. 2 shows the type of failure which was the most prevalent. The third type of failure, illustrated by sagger No. 3, occurred only in a few cases.

The average, the maximum, and the minimum temperatures of failure and porosities of the saggers prepared from the first 16 bodies listed in Tables 2 and 3 are as follows:

	Temperature of failure of saggers fired at—			
	1,230° C.		1,270° C.	
	Fine grog	Coarse grog	Fine grog	Coarse grog
Maximum ° C	760	860	400	450
Minimum do	445	500	630	710
Average do	580	675	495	540
Porosity per cent	26.2	26.2	25.4	25.1

These average values show that the coarse-grogged saggers resist thermal shock to a considerably greater extent than the fine-grogged saggers, although this difference is more pronounced in the saggers fired at 1,230° C. than those fired at 1,270° C. These results also show that the resistance to thermal shock decreases noticeably with the increased temperature of firing of saggers. Furthermore, a comparison of the average porosities of the fine and coarse grogged bodies indicates that, within the ranges of grog sizes and temperatures of firing studied, the porosity as determined does not give a true indication of the pore structure of the body.

Sagger bodies Nos. 9F, 9C, 10F, 10C, 12F, 12C, 13F, and 13C were prepared from two clays each and grog made from only one of the clays used in the respective bodies. The grog used in sagger mixes 9F, 9C, 12C, and 12F was prepared from that clay in the mix having the lower porosity after firing at 1,230° C., whereas bodies 10F, 10C, 13F, and 13C contained grog prepared from that clay in the body having the higher porosity after firing at 1,230° C. Furthermore, bodies Nos. 7F and 7C contain the same clays as 9F and 9C and bodies 13F and 13C contain the same clays as 14F and 14C. The results obtained in the thermal shock test indicate that saggers prepared with grog having a relatively high porosity show greater resistance to heat shock than do saggers containing grog having a low porosity. A summary of the average values obtained on the fine and coarse grogged bodies as well as those of the clays are as follows:

Average temperature of failure of saggers

Body Nos.	Type of grog in body	Prepared from—		Remarks
		Single clays	Blended clays	
		° C.	° C.	
7F and 7C	Equal parts high and low porosity	665	650	Same clays in bodies 7 and 9.
9F and 9C	Low porosity	665	605	
10F and 10C	High porosity	390	520	
12F and 12C	Low porosity	570	575	
13F and 13C	High porosity	435	655	Same clays in bodies 13 and 14.
14F and 14C	Equal parts high and low porosity	435	575	

Bodies Nos. 10 and 12, although compounded with different clays, illustrate the effect on the resistance to thermal shock of saggers containing either dense or porous grog. As shown, the average of the two failing temperatures of the saggers made from each clay used in body No. 10 was 390° C.; the saggers from the blended clays and a porous grog showed greatly increased resistance to failure. The temperature of failure in this case was 520° C. In the case of body No. 12 the average of the two failing temperatures of the saggers prepared from each clay was 570° C., whereas the average of the failing temperatures of saggers prepared from the blended clays and a dense grog was 575° C. Furthermore a comparison of the results obtained on body No. 7 with body No. 9 and also on body No. 13 with body No. 14 indicates that the sagger containing the greater percentage of porous grog shows the greatest resistance to heat shock.

Body No. 11F and body No. 11C are described in the section on "Linear thermal expansion." The average of the two failing temperatures of the saggers made from each of the constituent clays was 465° C., the average of the two failing temperatures of saggers prepared from the blended clays was 645° C. The reaction which occurred, incident to the burning of these two blended clays caused an unusual improvement in the thermal expansion of the blended clay sagger bodies (see fig. 2) and undoubtedly was partially the cause of the excellent resistance to failure shown by the saggers in the heat-shock test.

Bodies Nos. 1XF to 4XC, inclusive, representing the eight sagger mixes compounded with grog materials burned at 775° C. contain clays of the same laboratory key numbers as bodies Nos. 5, 6, 7, and 4, respectively. As indicated by the results in Table 2, this method of preparing grog does not improve the resistance of saggers to thermal shock. The grog is sufficiently soft to permit its disintegration during pugging of the sagger body which, in consequence, causes a body of finer texture with increased modulus of elasticity. At the same time the heat conductivity of the sagger is probably decreased, which also would be a factor in decreasing the resistance to failure in the heat-shock test.

Body 15S, which contains the grog and dust passing an 80-mesh sieve, was included to show the effect of extremely fine grog on the resistance to failure of a sagger in the thermal shock test. Both the porosity and transverse strength of this body are high, and the saggers failed at or below 350° C., an exceptionally low temperature. Body No. 8F containing the same body composition, but with graded grog, failed at 450° C.

Body 21SF (Table 3) was prepared from the same clays as bodies Nos. 4aF and 4aC, but the grading of the grog was varied as shown in the section on "Sagger body compositions." Although body 21SF contained 40 per cent of grog passing an 80 and retained on a 200-mesh sieve, the sagger failed in the air-quenching test at approximately the same temperature as body 4aF which contained no grog finer than that retained on an 80-mesh sieve. This would indicate that properly graded grog sizes, even as fine as those used in body 21SF, may be used to advantage to increase the mechanical strength of saggers.

Body No. 20SF was prepared from the same clays as bodies Nos. 6aF and 6aC, but with a fairly wide range of specially graded grog sizes. The saggers made from body 20SF failed at 460° C. in the heat-shock test, the approximate average failing temperature of saggers made from bodies 6aF and 6aC which failed at 400° and 590° C., respectively. The modulus of elasticity and transverse strength of body 20SF determined at 20° C. is also approximately the average of that obtained on bodies 6aF and 6aC. According to the data given in Table 6, the plastic flow of body 20SF under a load of 240 lbs./in.^{2} is slightly less than that of either body 6aF or 6aC. It would, therefore, appear from the limited data available that the use of grog, graded into as many as six sizes, is of no outstanding advantage in a sagger body when compared with bodies using three sizes of graded grog.

The data show that the individual saggers in any one set of five fired at 1,230° C. failed in the quenching test within 100° C. or less of one another in 32 out of a total of 37 bodies, and those fired at 1,270° C. failed within 75° C., or less, of one another in 23 out of a total of 26 bodies.

7. RELATION BETWEEN POROSITY AND DUNTING

As indicated by the following table of averages of temperatures at which saggers failed in the air-quenching test and the porosities of the fired sagger bodies, it is advantageous to keep the porosities of these bodies below 25 per cent. The bodies were separated into two

groups, according to whether the porosity was greater or less than 25 per cent:

Saggers fired at—	Average temperature of failure	Porosity
° *C.*	° *C.*	*Per cent*
1,230	675	20.7
	565	31.2
1,270	590	19.5
	455	31.2

Sufficient data are not at hand to warrant any conclusions as to the lowest permissible porosity compatible with the longest sagger life.

8. EFFECT OF THERMAL EXPANSION ON DUNTING

Grouping the sagger bodies fired at 1,230° C. into two classes according to whether saggers prepared from them failed at temperatures above or below 600° C. and averaging the temperatures at which they failed as well as the coefficients of expansion of each group from 20 to 250° C. gives the following:

Group	Average failing temperature	Average coefficient of expansion
	° *C.*	$\times 10^{-6}$
I	695	6.1
II	525	8.2

9. MODULUS OF ELASTICITY, EXPANSION, TRANSVERSE STRENGTH, POROSITY, AND RESISTANCE TO DUNTING

An empirical relation, combining the three factors (1) modulus of elasticity, (2) linear thermal expansion, and (3) transverse strength, which was suggested as indicating the relative resistance to failure due to thermal shock, was given in Report III.[11] The sagger bodies referred to in that report contained grog which had been graded alike for all mixtures. Substituting the data obtained in the present work in that formula, it was found that the factors R so computed did not satisfactorily indicate the relative resistance to thermal shock actually obtained. Changing the formula to include the porosity of the body overcame this discrepancy. This may be from the fact that the thermal conductivity of the body probably has a significant effect on its resistance to heat shock. Since it is reasonable to assume that pores affect conductivity, porosity might be introduced into the for-

[11] See footnote 1, p. 420.

mula and more consistent values of R obtained. Consequently the formula is altered as follows:

$$R=\frac{M}{E.e.P}$$

where

R = factor indicating relative resistance of a sagger to failure,
M = modulus of rupture,
E = modulus of elasticity,
e = coefficient of linear thermal expansion,
P = porosity.

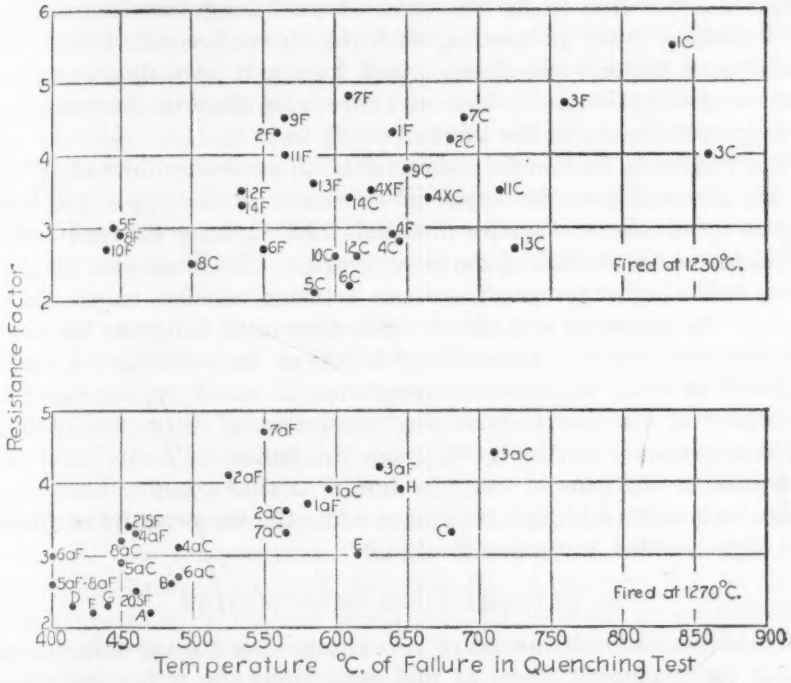

FIGURE 9.—*Showing the resistance (R) of saggers, fired at either 1,230° or 1,270° C., to dunting*

Data used in computing the resistance factor were determined at 20° C., and the average coefficient of expansion was taken from 20° C. to the temperature at which the saggers failed in the air-quenching test

The resistance factors R, computed from the moduli of elasticity and rupture and porosity determined at 20° C. and the average coefficient of expansion for the range from 20° C. to the temperature at which the saggers failed in the heat shock test, are given in Tables 2 and 3 for the saggers fired at 1,230 and 1,270° C., respectively. R plotted against the failing temperature of the saggers in Figure 9 shows, in general, that the greater the numerical value of this factor the greater the resistance of the sagger body to heat shock. Values for R computed from the moduli of elasticity and rupture determined

at either 750° C. or the failing temperatures of the saggers in the heat-shock test and the average coefficient of expansion between 20 and 600° C. give a similar relation. Although the relation between the calculated resistance R and the life of the sagger as indicated by the quenching test is not as close as may be desired, the trend of the points in Figure 9 indicates such a relation. The irregularities in the trend of the points may be partially accounted for by the differences in fired properties resulting from unavoidable variations in the heat treatment which the saggers and specimen bars received. This difference in heat treatment was especially apparent in the case of the material fired at 1,230° C., the resistance factors for which show the greater irregularity. In addition, other properties, such as thermal conductivity and modulus of elasticity in shear, which have not been determined in these studies, undoubtedly have an appreciable effect on the resistance of saggers to failure in the thermal shock test.

The resistance factors for the majority of the bodies fired at 1,230° C. are grouped near the approximate center of the upper graph in Figure 9, whereas the bodies fired at 1,270° C. have grouped themselves to the bottom left of the lower graph. This illustrates that the firing at the higher temperature has a detrimental effect on the resistance of the sagger to heat shock. Since repeated firings at the same temperature appear to have similar effects on the properties of sagger bodies [12] as firing at higher temperatures, it would appear that the resistance of a sagger to heat shock is decreased after each heating cycle in service. In the lower graph the factor for body 7aF is an exception to the general trend for bodies in that group. The factor indicates a relatively high resistance while the temperature at which the saggers failed is comparatively low.

10. EXTREME FIBER DEFORMATION

The maximum deformation of the extreme fiber [13] is the deformation under the maximum stress at mid span along the upper and lower surfaces of the specimen. The outer fiber deformation values of the fired sagger bodies at various temperatures given in Tables 2 and 3 (columns headed "Computed outer fiber strain") are all computed by the following formula:

$$\left.\begin{matrix}\text{Maximum elongation per} \\ \text{unit length, per cent}\end{matrix}\right\} = \frac{\text{modulus of rupture}}{\text{modulus of elasticity}} \times 100$$

The values so obtained are an expression of the approximate flexibility of the materials. An examination of these data indicates that the flexibility of the bodies decreased (1) with increased temperature

[12] Data on the effect of repeated firing of sagger clays are published in Report I. See footnote 1, p. 420.

[13] A detailed discussion on maximum deformation (elongation) and why it is desirable to use the secant modulus of elasticity when computing the strain values at 1,000° C. may be found in Report IV of this investigation. See footnote 1, p. 420.

of firing and (2) as the temperature of the material is raised until plastic flow commences under the load applied.

11. COMMERCIAL SAGGER BODIES

The laboratory identification letters for the commercial sagger mixes are A to H, inclusive. The properties of the bodies as determined on specimen bars and experimental saggers fired at 1,270° C. (cone 11½–12) are given in Table 3. The resistance factors R, of these mixes, given in Table 3, are included with the others plotted in Figure 9. The resistance to failure in the thermal shock test of saggers, prepared from bodies C, E, and H, is noticeably greater than that of the saggers prepared from the other five bodies. The modulus of elasticity of each of these three bodies is less and the computed outer fiber strain is greater than those of the remaining bodies. The increased resistance to failure of the saggers made from these bodies is probably due to these favorable factors. The properties of these bodies appear as a whole to be similar to the properties of the coarse grogged experimental bodies prepared in the laboratory. Largely, because of the coarse sizes of grog used in the bodies, the fired strength and the modulus of elasticity are low. It is believed that a low modulus of elasticity is desirable in a sagger body.

Bodies C and D were furnished by the same manufacturer. Body C, developed after a study of experimental sagger bodies, shows a great improvement in resistance to thermal shock when compared with body D. The modulus of elasticity of body D is approximately twice that of body C and is probably one of the most significant properties affecting dunting of saggers in the heat shock test at comparatively low temperatures. These data are of especial interest since they demonstrate that increased life of saggers, due to their greater resistance to thermal shock, may be obtained by altering the sagger mixes in such a manner as to produce a structure of the fired ware having those properties effective in prolonging the life.

VI. SUMMARY

Five small saggers were made from each of 23 experimental bodies and 10 small saggers were made from each of 16 bodies. The 39 bodies were prepared from 15 different clays and grogs made from these clays. The majority of the bodies were made of two clays and grogs prepared from these clays, each combination of clays being made into two bodies, one prepared with coarse-graded grog and the other with comparatively fine-graded grog. The saggers were tested for resistance to heat shock after firing at either 1,230° or 1,270° C. Specimen bars were made to correspond with each set of saggers and fired simultaneously with the saggers. These bars were used for determining the linear thermal expansion from 20° to 1,000° C., porosity,

moduli of elasticity, and rupture at room and elevated temperatures, and plastic flow at 1,000° C. In addition, saggers and specimens from eight raw sagger bodies furnished by potteries were fired at 1,270° C. and tested.

The linear thermal expansion of the bodies fired at 1,230° C. shows that they may be classed as follows into three groups according to the expansion: That of the body may be (1) greater than that of either clay, (2) approximately equal to the average of that of the clays, (3) approximately equal to the clay having the lower expansion. A comparison of the expansion of the bodies prepared with the coarse sizes of grog against those prepared with the finer sizes of grog shows that in the majority of cases the coarse-grogged bodies have the lower expansion. A comparison of the thermal expansion of the sagger bodies with those of the clays contained in the bodies shows that of the total of 15 combinations, 12 had more desirable expansions than either one or both of the constituent clays.

A direct relation between modulus of elasticity and transverse strength of the bodies is shown. The modulus of elasticity increased more rapidly than the strength when the bodies were (*a*) fired at 1,270° C. as compared with 1,230° C., and (*b*) tested at increasing temperatures ranging from 20° to 750° C.

A relation between porosity and plastic flow of the bodies under load at 1,000° C. is indicated.

The results show that the resistance of saggers to thermal shock (1) decreases with increased temperature of firing of saggers, (2) is generally less for bodies having a porosity greater than 25 per cent when compared with those having a porosity less than 25 per cent, (3) is greater for saggers prepared with grog having a relatively high porosity than those containing grog of low porosity, and (4) is greater for bodies having a comparatively small and uniform rate of expansion below 250° C.

A study of the data indicates that the best sagger bodies found in this preliminary experimental study are those having the following properties: (1) Low modulus of elasticity, (2) high transverse strength, (3) porosity below 25 per cent, and (4) low and preferably uniform thermal expansion from 20° to 250° C. In addition, it was found that clays of low refractoriness may sparingly and advantageously be used to increase sagger life and that properties stated as (1) and (2) may be partially controlled by grading of grog sizes.

The modulus of elasticity, transverse strength, porosity and coefficient of expansion may be combined into an empirical formula which will give indications of the probable life of a sagger when subjected to repeated thermal shock.

WASHINGTON, January 9, 1929.

A SUPPRESSED-ZERO ELECTRODYNAMIC VOLTMETER

By F. K. Harris

ABSTRACT

An error is introduced into the reading of a deflecting instrument by inelastic yielding of the mechanism supplying the counter torque. This error, if large enough to affect precision, may be made negligible by keeping the instrument permanently deflected to one position and allowing only small changes in this deflection. For a voltmeter this procedure necessitates a variable multiplier which in turn introduces a special problem in temperature compensation. The present paper describes an attempt at the solution of these problems. The resulting instrument will measure alternating voltages between 20 and 300 volts at power frequencies to an accuracy of 0.01 per cent. An appendix discusses some difficulties encountered in obtaining a steady supply of alternating voltage and describes the methods used in eliminating the troubles.

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I. INTRODUCTION

The voltmeter to be described was developed to meet the need for an a. c. instrument of greater precision and sensitivity than can be secured with available portable voltmeters. Specifically, an instrument was needed in our laboratory to measure voltages from 50 to 300 volts at power frequencies to an accuracy of 0.01 per cent. To meet these requirements, particular consideration must be given to two sources of error: (1) The temperature coefficent of the instrument must be either very accurately known or be made negligible; (2) the effect of inelastic yielding of the restoring springs must be eliminated. While this second source of error is usually negligible

in the operation of deflecting instruments, it is always present, and in the case under consideration it is of primary importance.

In general, when any imperfectly elastic body is suddenly subjected to a load it suffers a certain deformation at once. Then, if the load is continuously applied, the deformation changes by an amount which is a function of the load applied, the duration of the load, and the previous load history of the body.[1] In the case considered, when a constant voltage is impressed on a voltmeter the deflection of the moving element changes to some extent as long as the voltmeter remains in the circuit. When the circuit is opened, the pointer does not return at once to the zero position which it had before the application of the voltage, but to a position a little above it; that is, the effective zero point has moved upscale. The voltage reading will therefore be in error because of this zero shift which depends upon the length of time the voltmeter has been left in the circuit and to a lesser extent upon the previous readings taken with the instrument.

If this zero shift is proportional to the amount of the deflection, its effect can be made as small as desired by keeping the instrument always deflected to the point where it is to be used, by calibrating it in this condition, and by allowing only such changes in the deflection as are small in comparison to the total deflection.[2]

This has been done with the voltmeter described below. The moving system is mechanically held at a fixed position and is free to move through only a small angle. In order that the moving element may swing away from the stop against which it rests when no current is flowing, a definite value of current must pass through the instrument. To measure voltages, an adjustable resistance is connected in series with the instrument. The procedure followed is to vary the series resistance until the indicator swings freely between its stops. The impressed voltage is then known if the total resistance of the measuring circuit and the current required to produce the chosen deflection are known.

II. DESCRIPTION

1. INSTRUMENT

An electrodynamic voltmeter constructed in the Bureau of Standards instrument shop in 1908 was used in the set-up to be described. The moving element has two coils astatically arranged, each of 100 turns of silk-covered copper wire, No. 34 A. W. G. The moving element is suspended by phosphor-bronze strips between two sets of fixed coils mounted in wooden blocks. The fixed coils have about 460 turns each of copper wire, No. 30 A. W. G. These coils are con-

[1] A. A. Michelson, Laws of Elastico-viscous Flow, Proc. Nat. Acad. Sci., 3, pp. 319-323; 1917. M D. Hersey, On the Theory of Irreversible Time Effects, J. Wash. Acad. Sci., 11, pp. 149-155; 1921.

[2] This procedure was suggested by Dr. H. B. Brooks.

nected in series astatically and in series with the moving coils. The resistance of the six coils and the suspensions all in series is about 110 ohms. The inductance of the instrument is about 58 millihenrys.

A damping vane is attached to the moving system below the lower moving coil and swings with small clearance in a sector-shaped box.

A light aluminum arm is rigidly mounted on the moving system, and its motion is limited by two stops mounted on the case of the instrument. The moving element is free to rotate through an angle of slightly less than 3° between the stops. The normal position of the moving element between the stops is such that the fixed coils and moving coils are very nearly at right angles to each other. Hence, the mutual inductance between the fixed coils and moving coils is nearly zero. In this instrument the rate of change of inductance with angle is a maximum for this position, and therefore the square law for the scale is closely followed for the small changes in angle allowed by the stops.

The free period of the instrument is about two seconds.

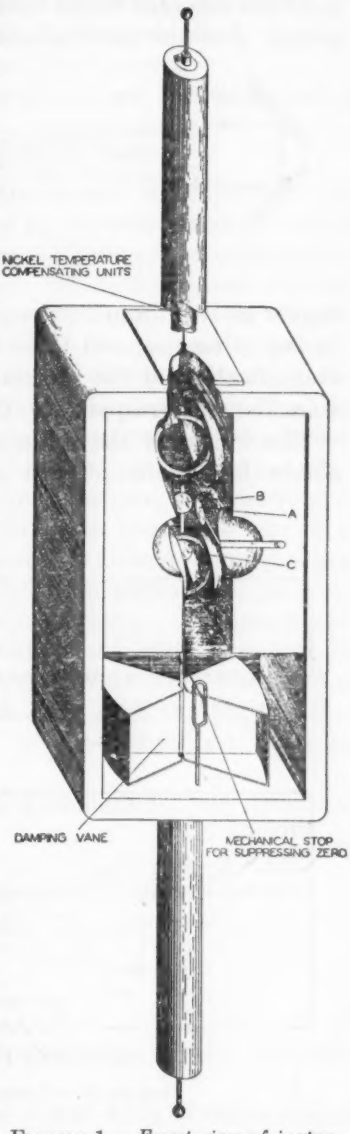

FIGURE 1.—*Front view of instrument with cover removed*

A, fixed mirror used with double optical lever.

B, moving mirror used with double optical lever.

C, mirror used with scale and telescope.

2. OPTICAL SYSTEM

For most purposes the mirror marked *C* in Figure 1 is used with the usual arrangement of telescope and scale to indicate deflections. The scale is mounted at a distance of 6 m from the instrument. It is 60 cm long and has its zero point in the center. The telescope is 4.5 m from the instrument. The entire free motion allowed in the moving system just sweeps the scale from end to end.

Another indicating system is used when further sensitivity is required. This is the double optical lever[3] shown in Figure 2. The two mirrors marked *A*, *B*, in Figure 1 are used. One mirror

[3] Attributed to Prof. L. Weber by H. Langner "Ueber eine Methode zur Messung kleiner Winkeldifferenzen," Zeits. für Instrumentenkunde, **6**, pp. 299-304; 1886.

is mounted on the case of the instrument and the other on the moving element. When these mirrors make an angle of about 90° with each other, a beam of light from a pinhole source incident on the moving mirror is reflected to the fixed mirror and thence to the observer's telescope. Another beam is reflected from the fixed mirror to the moving

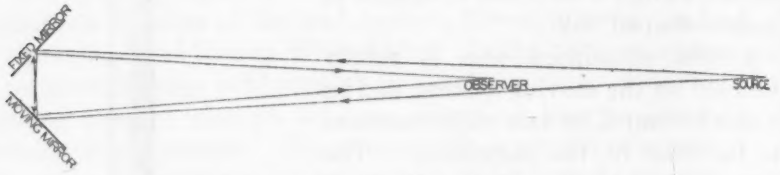

FIGURE 2.—*Double optical lever*

mirror and to the telescope. Thus, two images of the source are seen in the telescope, and their approach or separation gives a fourfold magnification of the angular motion of the moving element. Their coincidence corresponds to the position of standard deflection.

The image of the scale appears in the observer's telescope just above these points of light and is always used for preliminary adjust-

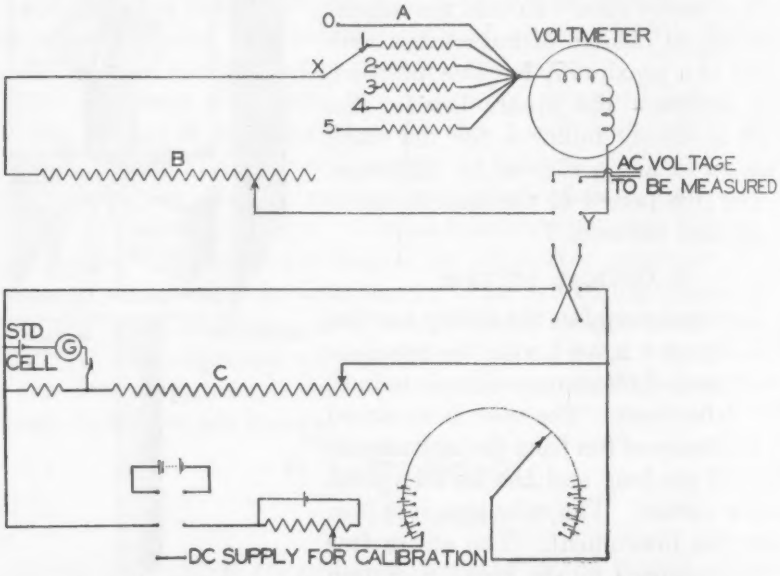

FIGURE 3.—*Schematic diagram of electrical circuits*

ment of the deflection as well as for all settings where the greater sensitivity is not required.

3. ELECTRICAL CIRCUITS

A schematic diagram of the electrical circuits is shown in Figure 3. The main series resistor *B*, used in making all voltage readings, is varied until the moving system assumes the standard deflection

described above. B is a 6-dial variable resistor of manganin wire so marked that one dial unit is 25 ohms.

When a calibration of the instrument is desired, the equivalent potentiometer C is thrown in parallel with the instrument and resistor B. The above-described standard deflection is then obtained simultaneously with a potentiometer balance on direct current.

The selector switch X and the resistors A are for temperature compensation.

4. TEMPERATURE COMPENSATION

In an electrodynamic milliammeter the torque is proportional to the square of the current and is balanced by the countertorque of the phosphor-bronze suspensions. Since the stiffness of the suspensions decreases approximately 0.04 per cent per degree centigrade increase of temperature, the reading will increase 0.02 per cent per degree. If the milliammeter plus added resistance is to be used as a voltmeter, this effect of temperature will be compensated if the resistance of the voltmeter increases 0.02 per cent per degree. Ordinarily this may be done by using a series resistor of negligible temperature coefficient having a resistance about nineteen times that of the copper coils.[4]

The suppressed-zero voltmeter, however, has two features requiring special consideration. The resistance of the measuring circuit is proportional to the voltage being measured. Hence, compensation merely by the addition of series resistance of negligible temperature coefficient is possible for only one value of voltage. Expansion and warping of the various parts of the instrument and its case with changing temperature may cause a shift of $(dD/d\theta)\,\delta\theta$ in the position of the suppressed zero. Because of this zero shift the temperature coefficient of the instrument can not be predicted, but must be measured.

Equating torques acting on the moving element for any temperature θ

$$I^2\,dM/d\phi = U_o\left(1+\frac{dU/d\theta}{U_o}\delta\theta\right)D_o\left(1+\frac{dD/d\theta}{D_o}\delta\theta\right)$$

$$I=\sqrt{\frac{U_o D_o}{dM/d\phi}}\left(1+\frac{1}{2}\left[\frac{dU/d\theta}{U_o}+\frac{dD/d\theta}{D_o}\right]\delta\theta\right)$$

$$=K_o(1+\gamma\,\delta\theta)$$

where

U_o is the elastic constant of the suspensions at the temperature θ_o,

D_o is the deflection from the effective zero at θ_o to the standard position of the moving system,

$dM/d\phi$ is the rate of change of mutual inductance with angle,

γ is the combined effect of the temperature coefficients of the elastic constant and the zero shift, and

$\delta\theta$ is the departure from the temperature θ_o.

[4] H. B. Brooks, The Accuracy of Commercial Electrical Measurements, Trans. A. I. E. E., **29**, Pt. 1, p. 516; 1920

Also the resistance of the circuit at any temperature is

$$R = R_E\,(1+\alpha\delta\theta) + R_S$$

where

α is the temperature coefficient of resistance of copper,
R_E is the resistance of the instrument at θ_o, and
R_S is the resistance of the series multiplier.

Consequently the voltage is, neglecting a second order term,

$$V = IR = K_o\,(R_E + R_S)\left(1+\left[\frac{\alpha R_E}{R_E+R_S}+\gamma\right]\delta\theta\right)$$

and the temperature coefficient of the instrument, defined as $\frac{1}{V}dV/d\theta$, is for this voltage

$$\epsilon = \frac{\alpha R_E}{R_E+R_S}+\gamma$$

The compensation of the voltmeter here described is found to be perfect when about 10 per cent of the total resistance is of copper (at about 44 volts). Then, since $\alpha = 0.4$ per cent, $\gamma = -0.04$ per cent. It should be noted that half of γ is due to a shift of the effective zero with temperature.

It was desirable to have the instrument compensated for temperature throughout its useful range up to 250 volts. It was therefore necessary that the additional series resistance used in measurements above 44 volts have the correct temperature coefficient. If β is the temperature coefficient of the added series resistance material (R_N) used, then the temperature coefficient of the instrument becomes

$$\epsilon = \frac{\alpha R_E + \beta R_N}{R_E+R_N+R_S}+\gamma$$

Nickel wire was chosen for this purpose both because of its high resistivity and its large temperature coefficient, namely, 0.6 per cent per degree centigrade.

The final expression for the temperature coefficient of the instrument is then

$$\epsilon = \frac{0.004R_E + 0.006R_N}{R_E+R_N+R_S} - 0.0004$$

This compensating resistance should vary in temperature with the suspensions and coils of the instrument and should be insulated against outside temperature changes to the same degree. A single layer of nickel wire was therefore wound around the brass tubes which protect the suspensions. Half of this wire is wound around the lower suspension tube and half around the upper tube. It is protected against outside temperature changes by a layer of cotton batting which is in turn inclosed in brass tubes.

The suspensions, moving coils, fixed coils, and compensating resistance are thus all inclosed within the case of the instrument and are well

insulated against sudden outside temperature changes. Their temperatures will, therefore, change very slowly and, under the conditions usually encountered in operation, will remain substantially equal.

The compensating resistance is wound in five sections which can be connected in the circuit by the dial switch X. (Fig. 3.) An additional constantan resistance is incorporated in each section to make the total resistance between points (X) and (Y) (fig. 3) 500 ohms at 20° C. for any position of the dial switch from 1 to 5.

The positive temperature coefficient of resistance of the entire electrical circuit up to the selector switch Y (fig. 3) must be equal to the combined effect of the zero shift and the change in stiffness of the suspensions for perfect compensation. For any particular resist-

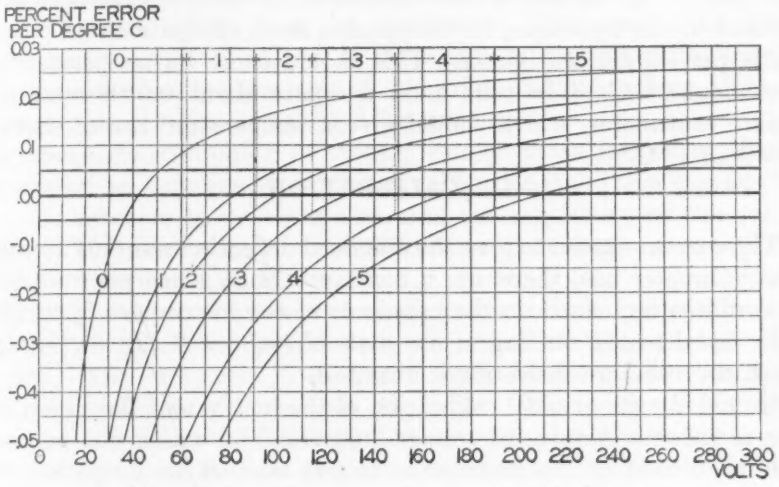

FIGURE 4.—*Temperature compensation of voltmeter*

Vertical dotted lines show voltage range through which each compensating unit (0-5, fig. 3) is to be used.

ance of nickel wire used there is only one value of total resistance (and one value of voltage)[5] for which the two temperature coefficients are numerically equal. Then for this particular value of resistance and voltage the temperature coefficient of the instrument is zero. For smaller resistances and voltages the temperature coefficient will be negative and for larger values will be positive. For a considerable range it will be very small. By properly choosing a number of such points the temperature coefficient of the instrument can be made negligible throughout its useful range.

The actual value of the temperature coefficient of the instrument as a function of the voltage being measured is shown for the several dial settings in Figure 4. It will be seen from this figure that by

[5] The voltage is measured by varying the total resistance of the instrument.

proper selection of the compensating unit the temperature coefficient can be made less than 0.01 per cent per degree centigrade for voltages between 30 and 300 and less than 0.005 per cent per degree centigrade between 70 and 260 volts.

In view of the fact that calibration of the instrument is made frequently when accurate measurements are being made and since only such temperature changes as take place within the instrument case between the time of reading and the subsequent calibration affect the value of the reading, this small temperature coefficient is quite negligible.

The self-heating of the instrument is small. With the current chosen (0.04 ampere) to give the standard deflection, it amounts to less than 1° C. for continuous operation. Neglecting the heat conduction to the terminals, the suspension must dissipate about 0.0025 watts per square centimeter. This should cause its temperature to rise about 1° C. The coils must dissipate about 0.0008 watt per square centimeter, which should give a temperature rise of slightly less than 1° C.[6]

III. CALIBRATION

The current chosen to give the standard deflection was 0.04 ampere. The voltmeter has, therefore, a resistance of 25 ohms per volt, and the voltage impressed on the terminals of the instrument is numerically equal to the reading of the dials of resistor *B* (fig. 3) plus 20, when the standard deflection is obtained.

In making the original calibration of the instrument the procedure was as follows: A value of voltage (100 volts) for which the temperature coefficient of the instrument is zero was set on the potentiometer *C* (fig. 3), and resistor *B* was set to read 80 dial units. Then, with the potentiometer balanced, the suspension clamps of the instrument were rotated until the moving system swung free between its mechanical stops and the standard deflection was indicated by the double optical lever (fig. 2). The suspension clamps were then tightened in this position.

When the voltage was removed from the instrument, the moving system rotated through 1.5° and came to rest against the lower stop. The total rotation from the normal zero position of the moving system was about 60°.

In measuring a voltage it is only necessary to vary the resistance of resistor *B* until the standard deflection is obtained. The voltage is then the reading of the dials of *B* plus 20.

---

[6] The value given in Whittaker's Electrical Engineer's Pocket Book, p. 111, 3d ed., for shellacked cotton bobbins is equivalent to 0.00086 watt per square centimeter per degree centigrade. The dissipation of 0.0025 watt per square centimeter per degree centigrade for the suspension seems reasonable on the basis of unpublished data at hand.

When a more accurate value of voltage is required, the compensating dial A (fig. 3) is set to the position which, for the voltage to be measured, most nearly reduces the temperature coefficient to zero. Resistor B is next set in the usual manner. Then, without changing the setting of B, a direct voltage is substituted for the unknown alternating voltage and is varied until the standard deflection is again obtained. Holding this voltage constant, the potentiometer is then balanced. In order to correct for any lack of astaticism in the instrument, the above procedure is duplicated after reversing the direction of the direct current through the fixed coils and moving coils and the mean of the two potentiometer readings is taken.

The required value of alternating voltage differs from the mean of the potentiometer readings only in so far as the a. c. impedance of the instrument differs from its resistance. The error from this source is inversely proportional to the square of the voltage measured and amounts to 0.004 per cent at 100 volts and 60 cycles. It can, therefore, be considered negligible for most work.

A precise determination of voltage can be made in two or three minutes by an experienced operator. The determination can easily be made accurate to 0.01 per cent, and the sensitivity of the voltmeter is sufficiently great that differences in voltage as small as 0.002 per cent may be detected.

Where a number of successive readings are to be taken within the range of a volt or so, the following procedure has been found convenient. The voltmeter is calibrated with reversed direct voltage at some convenient value within the range. The change in voltage necessary to produce a deflection of 10 cm on the scale is determined. Then, with resistor B set at the mean value found in the calibration, the deflection may be read for small changes in the voltage. The corresponding voltages are determined from the scale calibration just made. The scale calibration will vary with the voltage being measured, being about 0.01 volt per centimeter at 20 volts and 0.1 volt per centimeter at 200 volts.

IV. ZERO-DRIFT ERROR

Drift measurements were made before the suppressed-zero arrangement was added to the instrument. A current of 0.046 ampere was passed through the coils and the sudden deflection [7] was noted. The current was changed when necessary to maintain the deflection. The results of this test are shown in Figure 5.[8] Equivalent drift

[7] By sudden deflection is meant the deflection which the moving system indicates as soon as it comes to rest after the voltage is impressed.

[8] The data from which Figure 5 is plotted were supplied by Dr. F. B. Silsbee. The writer wishes to express his appreciation for this and for Doctor Silsbee's many helpful suggestions during the course of the investigation.

is plotted as ordinates against time as abscissa. It may be noted that after the voltage has been impressed for five minutes the total drift is 0.04 per cent of the initial deflection. Hence, the rate of drift is approximately 0.01 per cent per minute initially. After one-half hour the total drift is 0.2 per cent of the initial deflection. There

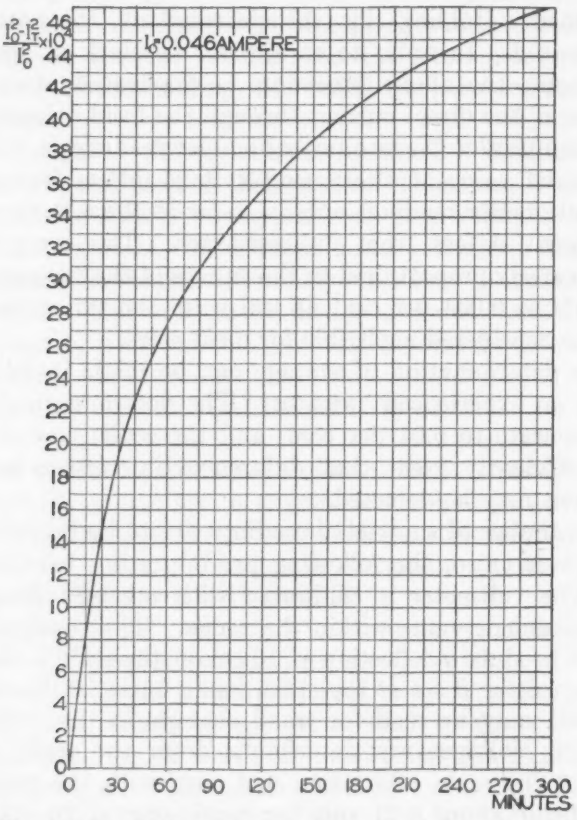

FIGURE 5.—*Drift measurements starting from unstressed condition*

The total change in deflection indicated is 0.47 per cent of the initial deflection represented by the point, (0,0).

is no indication from the data taken that this drift ceases even after a number of days.

With the stops of the suppressed zero arrangement in place, the angular motion from the stop necessary to obtain the standard deflection is about 2 per cent of the sudden deflection on which Figure 5 has been based. If it be assumed that the drift is proportional to the amount of the sudden deflection, then the drift with the zero suppressed should be about 0.004 per cent during the first half hour after deflection takes place.

A test of this argument was made recently after the moving system had been continuously deflected to within 1.5° of its standard deflection (60°) for more than a year. A voltage was applied which brought the moving system from its mechanical lower stop to the standard deflection. This voltage was changed when necessary to maintain the standard deflection. The change in voltage was noted over a period of one-half hour from the time of its application. It amounted to about 0.003 per cent. This drift is nearly equivalent to the smallest change that can be detected with certainty and is entirely negligible. It can therefore be said that drift errors have been eliminated in the instrument.

An analysis was recently made of a large number of readings taken with the instrument over a period of 100 days. It showed a gradual and apparently uniform drift which amounted to 0.2 per cent for the whole period. In other words, the current required to produce the standard deflection was 0.2 per cent less at the end of the period than at the beginning.

Whether this difference is due to slipping of the suspension clamps, or to inelastic yielding in the suspensions or in the soldered joints at the suspension terminals, has not been determined. It seems probable, however, that the inelastic yielding, which amounts to a considerable item immediately after deflection, continues over a period of years at a very slow rate.

V. USES OF THE INSTRUMENT

The principal application of the instrument described above has been for the measurement of the secondary voltage of potential transformers. The primary voltage is then known as accurately as the ratio of transformation is known; that is, to within about 0.01 per cent at best. It has been found useful in various experiments where it was necessary to hold an alternating voltage constant within narrow limits, since it will detect and follow variations in voltage that can not be seen with the best portable instruments.[9] It has also been used in the calibration of high-grade portable voltmeters.

The field of usefulness is restricted to precision measurements on account of the time consumed in making readings and the limited scale range of deflections. The scale range is about 3 per cent of the voltage measured, viz, 0.6 volt at 20 volts and 6 volts at 200 volts.

VI. SUMMARY

An astatic electrodynamic voltmeter has been described in which errors arising from zero drift have been eliminated and whose temperature coefficient has been reduced to a negligible value. By using a

[9] See Appendix for note on constant alternating voltage supply.

very long optical system to indicate deflections, differences of voltage as small as 0.002 per cent can be readily observed.

A d. c. potentiometer is built into the set-up so that the value of any alternating voltage within the range of the voltmeter can be readily determined in terms of the electromotive force of a standard cell. Measurements can be made on the instrument to an accuracy of 0.01 per cent for voltages between 20 and 300 volts.

VII. APPENDIX

1. NOTE ON CONSTANT VOLTAGE SUPPLY [10]

Considerable trouble has been experienced in obtaining alternating voltages which were sufficiently constant for precision work. The sensitivity available in the above-described instrument made it very useful for the study of this problem.

The source of a. c. supply studied was a direct-coupled motor-generator set of two 60-cycle, 5 kv-a generators and a 250-volt d. c. driving motor. The d. c. motor was supplied by a large storage battery.

In the course of this study a number of causes of trouble were found that could be practically eliminated. Since the voltmeter is sensitive to changes in supply voltage which may be produced by (1) variation in excitation, (2) variation in electrical load, and (3) variation in speed of the motor-generator set, a systematic investigation with this voltmeter disclosed the following undesirable conditions:

(*a*) Large variations in the exciting current in the rotating field windings were found to be a result of variations in brush contact resistance at the slip ring. Consequently, each brush was replaced by four smaller metal-graphite brushes with individual springs, operating independently in separate slots in the modified brush rigging.

(*b*) Variation in load was found to be caused in one case by a poorly-soldered stranded-wire connection of leads to the machine, in another by a loose fuse, and in another by an intermittent shorting of two turns of a large inductance coil.

(*c*) Variation in speed of the motor was found to be the result of variation of commutator-brush resistance (which was also improved by brush subdivision) and of variable friction in the bearings which was remedied by realignment and by replacement of bearings. Still further improvement resulted from driving the set by one generator operating as a synchronous motor in place of the d. c. motor and storage-battery drive. This synchronous motor was supplied from a 3-phase generator of much greater moment of inertia, which in turn was driven by a d. c. motor supplied by the large storage battery.

[10] The work described in this section was done principally by Dr. F. M. Defandorf.

It has been found necessary to give frequent attention to the slip rings in order to keep them as smooth and clean as possible. The subdivided brushes used are of the copper-graphite variety and show a smaller variation in contact resistance if additional lubricant is not used on the slip rings.

2. NOTE ON DIRECT-CURRENT SUPPLY FOR CALIBRATION OF SUPPRESSED-ZERO VOLTMETER

For convenient calibration it is essential to have a source of direct voltage which is continuously variable within wide limits. This has been obtained as shown in Figure 3. A remotely controlled dial selector switch furnishes voltage in 10-volt steps up to 200 volts from a storage battery. In series with this supply is a smaller voltage (12 volts) connected to a rheostat of about 25 ohms resistance. The drop between one end and the slider of this rheostat provides for the fine adjustment necessary in making settings on the voltmeter. In case a higher voltage is needed another storage battery is introduced in the line in series with the other two.

This system was chosen for supplying the direct voltage for the instrument because the calibration is facilitated if the resistance of the d. c. source is low in comparison to the resistance of the set-up. It will be noted that, except for the fine adjustment which has a resistance of 2 ohms per volt, the only resistance in the source is the internal resistance of the storage batteries used for supply and that of the leads to the instrument.

WASHINGTON, March 25, 1929.

TWO ISOMERIC CRYSTALLINE COMPOUNDS OF d-MANNOSE WITH CALCIUM CHLORIDE[1]

By J. K. Dale[2]

ABSTRACT

A crystalline double compound of mannose and calcium chloride having the formula $C_6H_{12}O_6 \cdot CaCl_2 \cdot 4H_2O$ has been prepared. The compound showed an extremely rapid initial rate of mutarotation from about $[\alpha]_D = -30$ to a positive maximum followed by a slow decrease to a constant value. The sugar constituent of this compound is a new form of mannose, and application of Hudson's rule indicates that it is the beta form corresponding in ring structure with α-mannose of $[\alpha]_D = +30$. A second isomer having the formula $C_6H_{12}O_6 \cdot CaCl_2 \cdot 2H_2O$ was obtained by evaporating an alcoholic solution of the above compound on a water bath. Its initial and final specific rotation and course of mutarotation indicate that it is a double compound of the well-known β-mannose of $[\alpha]_D = -17$ with calcium chloride. The second compound, but not the first, could be acetylated to give a good yield of β-mannose penta-acetate.

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I. INTRODUCTION

Crystalline compounds of the sugars with inorganic salts, a number of which are known,[3] have hitherto been of little interest in the advancement of our knowledge concerning the structures of the sugars. However, the important position which mannose holds in relation to structural studies makes the preparation and study of any

[1] The writer has arranged with Dr. C. S. Hudson that the present communication be included as No. 19 in the series entitled "Relations Between Rotatory Power and Structure in the Sugar Group."

[2] National research fellow.

[3] v. Lippmann, Chemie der Zuckerarten, 3d ed., pp. 549 and 884.

of its compounds or derivatives of unusual interest. Dr. C. S. Hudson informed the author that he had observed the formation of crystals in a solution of mannose and calcium chloride and suggested that the writer prepare and investigate the compound whose existence in a crystalline state had been thus indicated. This proposal led to far more interesting results than had been anticipated. The double compound of mannose and calcium chloride which was obtained showed mutarotation, but the course of the mutarotation was of an

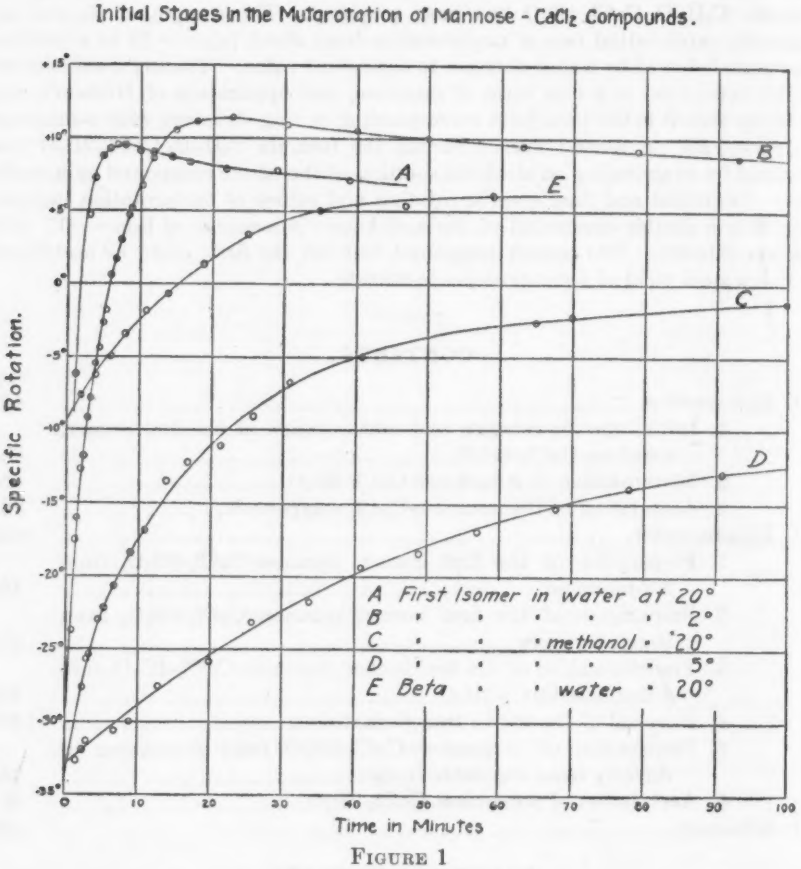
Initial Stages in the Mutarotation of Mannose - $CaCl_2$ Compounds.
Specific Rotation.
Time in Minutes
A
B
C
D
E
A First Isomer in water at 20°
B " " " " " 2°
C " " " methanol " 20°
D " " " " " 5°
E Beta " " water " 20°

FIGURE 1

unusual character differing from that of any known sugar. Secondly, by evaporating an alcoholic solution on a water bath the compound was transformed into a second modification, isomeric with the original. Subsequently it was found that either isomer could be made at will from mannose and calcium chloride, or even directly from hydrolyzed vegetable ivory, depending upon the solvent and the temperature at which crystallization took place. The first isomer crystallizes from a concentrated aqueous solution of mannose and calcium chloride at room temperature, while the second crystallizes

from an alcoholic solution during evaporation on a boiling water bath. The isomer crystallizing from water at room temperature showed a calcium and chlorine content, loss of weight on drying, and specific rotation at equilibrium corresponding to the formula $C_6H_{12}O_6 \cdot CaCl_2 \cdot 4H_2O$. As its initial specific rotation and course of mutarotation, in the early stages at least, do not permit a correlation with either of the known forms of mannose, it will subsequently simply be designated as the "first isomer." The second isomer, crystallizing from alcohol at the temperature of a boiling water bath, showed a calcium and chlorine content corresponding to the formula $C_6H_{12}O_6 \cdot CaCl_2 \cdot 2H_2O$. Its initial specific rotation and course of mutarotation correlate it with β-mannose of initial $[\alpha]_D = -17$; hence, it will be designated as β-mannose$\cdot CaCl_2 \cdot 2H_2O$.

1. INITIAL SPECIFIC ROTATION AND MUTAROTATION OF THE FIRST ISOMER, MANNOSE$\cdot CaCl_2 \cdot 4H_2O$

The first observations of the direction of the mutarotation of this compound indicated that the optically active component was α-mannose. However, an extrapolation of its mutarotation curve to zero time showed an initial specific rotation, calculated to a mannose basis, of $[\alpha]_D = +20$, whereas Levene [4] had found $[\alpha]_D = +30$ for α-mannose. Subsequent attempts to obtain readings more quickly after making the solution gave the unexpected result that the anticipated normal mutarotation was preceded by an extremely rapid change from a negative value, far below even that of β-mannose, to a positive maximum. From this maximum the rotation fell at a rate comparable with that of α-mannose. At 20° in aqueous solution the initial change was too rapid to be accurately measured. At 2° it was still rapid, but could be followed with sufficient precision to permit a close estimation of the initial value. In Tables 1 and 2 are recorded the mutarotation data for this compound in aqueous solution at the temperatures of 20° and 2°, respectively. The curves *A* and *B* of the figure are plotted from these readings.

The later part of the mutarotation, decreasing from the maximum to an equilibrium value, appears to be unimolecular, and the constant found at 20°, $k_1 + k_2 = 0.025$, is of the same order of magnitude as that given by Hudson and Sawyer for β-mannose [5] (0.019), and Levene [6] has shown that α-mannose has the same rate of mutarotation as the beta form. Furthermore, if this portion of the curve is extrapolated to zero time the initial specific rotation thus estimated is not far removed from that of α-mannose. These facts constitute evidence that this stage of the mutarotation is the passing of α-mannose to the equilibrium state of mannose solutions.

[4] J. Biol. Chem., **57**, p. 329; 1923; **59**, p. 129; 1924.
[5] Hudson and Sawyer, J. Am. Chem. Soc., **39**, p. 475; 1917.
[6] See footnote 4.

TABLE 1.—*Mutarotation of the first isomer, d-Mannose·$CaCl_2$·$4H_2O$, in water*

[1.7437 g compound in 25 ml solution. Tube length, 2 dm. $T=20°\pm0.5°$]

Time after making solution (minutes)	$[\alpha]_D^{20}$ of compound	Time	$k_1+k_2=\frac{1}{T}\log\frac{r_0-r\infty}{r-r\infty}$
1½	−6.22		
3	+4.73		
4	+7.21		
5	+8.74		
6	+9.20		
7	+9.46		
8	+9.46	0	
10	+9.08	2	0.032
12	+8.95	4	.022
14½	+8.64	6½	.024
17	+8.33	9	.026
22	+7.80	12	.028
29	+7.71	21	.021
39	+7.09	31	.028
∞	+6.72		
Average			.025

TABLE 2

[2.856 g compound in 25 ml solution. Tube length, 2 dm. $T=2°\pm0.5°$]

Time after making solution (minutes)	$[\alpha]_D^{20}$ of compound	Time	$k_1+k_2=\frac{1}{T}\log\frac{r_0-r\infty}{r-r\infty}$
¾	−23.68		
1¼	−17.60		
1½	−15.97		
2	−12.75		
2¼	−11.83		
3	−9.10		
3½	−7.89		
4	−5.46		
4½	−4.55		
5	−2.73		
5½	−1.82		
6	+.61		
6¾	+1.82		
7½	+3.03		
8¼	+4.85		
9	+5.16		
10¼	+6.68		
12	+8.62		
15	+10.50		
18	+11.05		
23	+11.35	0	
30½	+10.93	7½	0.0052
40	+10.42	17	.0054
50	+10.00	27	.0053
63	+9.42	40	.0054
79	+9.10	56	.0048
93	+8.62	70	.0051
111	+7.71	88	[.0068]
130	+7.10	107	[.0085]
147	+6.68	124	[.0115]
∞	+6.50	∞	
Average			.0052

The initial rapid increase in rotation deserves special attention. The possibility exists that this change is due to a dissociation of the mannose calcium chloride compound. This explanation appears unlikely, however, because no change in polarization due to a slow dissociation of sugar and salt has been observed in other compounds of this nature.[7] It appears to be more likely that this change is due to a rapid rearrangement of a new form of mannose to the alpha modification. If this is true, the initial specific rotation of this new form of mannose becomes of special interest. Extrapolation of the mutarotation curve *B* to zero time shows the initial specific rotation of this compound to be about -30 and hence for the mannose constituent $[\alpha]_D = -60$. Owing to the extreme rapidity of the early stages of the polarimetric change this figure is uncertain by several degrees.

The rate of the polarimetric change of the first isomer in methanol is much slower than in water; hence in this solvent the course of the change could be followed with more precision and the initial specific rotation determined with more accuracy. Curves *C* and *D* show the early stages of the mutarotation of this compound at the temperatures of 20° and 5°, respectively. Extrapolation of these curves to zero time gives the values for the initial specific rotation at these two temperatures as -34 and -33, and, hence for the mannose constituent, $[\alpha]_D = -68.6$ and -66.5. The final or equilibrium value for the specific rotation in this solvent was found to be $+4.0$ and $+4.8$, an average of $+4.4$, which calculated to a mannose basis equals $+8.9$.

C. S. Hudson [8] has produced evidence from theoretical considerations based upon the principle of optical superposition that the two known crystalline forms of mannose are not a true alpha and beta pair having the same ring structure, but that the form with an initial specific rotation $+30$ is the alpha form of a 1, 5 ring structure, while the form showing $[\alpha]_D = -17$ is the beta form of a 1, 4 ring structure. He has further calculated the specific rotations to be expected for the missing members of these 2 ring structures and predicts the value for the β form of the 1, 5 ring structure to be $-65°$ in water solution. The initial specific rotation of a new form of mannose, occurring as a crystalline double compound with $CaCl_2$, is here shown to be not far from -60 in aqueous solution. The close agreement of this measured initial specific rotation of the new form of mannose with one of Hudson's calculated values, -65, lends strong experimental support to his view that the well-known crystalline forms of mannose possess different ring structures, and as a corollary it follows that the mannose

[7] The author has prepared in crystalline form calcium chloride compounds of arabinose, xylose, and fructose, and also the well-known compound of sodium chloride and glucose. Each of these substances shows a normal mutarotation comparable with that of the sugar constituent. The data will be published in a subsequent article.

[8] C. S. Hudson, J. Am. Chem. Soc., **48**, pp. 1425 and 1434· 1926.

constituent of the crystalline compound here described is the beta form of the sugar, corresponding in ring structure with alpha mannose of initial specific rotation +30. If this view is correct, the initial mutarotation must be explained as a rapid conversion of the beta form of one ring structure to the corresponding alpha form. The subsequent slower polarimetric change must then be considered to be an establishment of equilibrium between forms of different ring structures.

2. MUTAROTATION OF β-MANNOSE·$CaCl_2$·$2H_2O$

This compound, which was first obtained by concentrating an alcoholic solution of the first isomer on a boiling water bath, was characterized by a normal mutarotation in aqueous solution, as shown in Table 3 and by curve *E*. The mutarotation constant, k_1+k_2, at 20° was found to be 0.024, a value essentially the same as the constant found for the latter stage of the mutarotation of the first isomer (0.025) and slightly higher than the value, 0.019, found for β-mannose[9] at this temperature.[10] The final specific rotation, +6.73, and the extrapolated initial specific rotation, −9.0, correspond to +12.2 and −16.2, respectively, for the mannose constituent. Thus, this isomer is apparently a compound of $CaCl_2$ with the well known β-mannose, of $[\alpha]_D = -17$.

3. ACETYLATION OF THE MANNOSE·$CaCl_2$ COMPOUNDS

β-mannose·$CaCl_2$·$2H_2O$ may be of utility in the synthesis of mannose derivatives because it can be directly acetylated to give a good yield of β-mannose pentaacetate. This may be of timely importance, for pure β-mannose has recently become difficult to obtain, at least in some laboratories. Levene [11] states that after having once prepared α-mannose subsequent recrystallizations of impure mannose from alcohol invariably gave this form. The author recrystallized at intervals several lots of impure mannose in the research laboratory of St. Andrews University. At first β-mannose was obtained, but unexpectedly one lot appeared as the alpha isomer, and thereafter the recrystallized product always consisted of this form. It is true that alpha mannose can be acetylated [12] to give alpha mannose pentaacetate, but the yield is not more than 20 per cent of the theoretical which is far from satisfactory. On the other hand, β-mannose or

[9] Hudson and Sawyer, J. Am. Chem. Soc., 39, p. 475; 1917.

[10] The difference between the value $k_1+k_2=0.024$ found for β-mannose $CaCl_2$·$2H_2O$ and the value $k_1+k_2=0.019$ found by Hudson and Sawyer for β-mannose is too great to be attributed to experimental error. It is more likely that the rate of mutarotation of the mannose constituent of β-mannose·$CaCl_2$·$2H_2O$ is accelerated by the presence of $CaCl_2$ in the solution. In confirmation a mutarotation experiment was made upon β-mannose dissolved in water and a second one upon β-mannose dissolved in a $CaCl_2$ solution of such strength that mannose and $CaCl_2$ were present in equimolecular proportions. Mannose in water alone showed $k_1+k_2=0.020$, while in the $CaCl_2$ solution it showed $k_1+k_2=0.025$.

[11] See footnote 4, p. 461.

[12] Levene, J. Biol. Chem., 57, p. 329; 1923.

β-mannose·$CaCl_2$·$2H_2O$ readily yields on acetylation 60 per cent or more of the theory. The first isomer (mannose·$CaCl_2$·$4H_2O$) on acetylation with acetic anhydride and pyridine in an ice bath gave a sirupy gum which after long standing in an ice chest yielded only a few crystals of β-mannose pentaacetate.

TABLE 3.—*Mutarotation of β-mannose·$CaCl_2$·$2H_2O$ in water*

[3.0146 g compound in 25 ml solution. Tube length 2 dm. $T=20°\pm0.5°$]

Time after making solution (minutes)	$[\alpha]_D^{20}$ compound	Time	k_1+k_2
2	−7.70	0	
4	−6.33	2	0.022
6	−5.02	4	.025
8	−3.47	6	.025
11	−1.97	9	.024
14	−.68	12	.024
19	+1.20	17	.024
25	+3.30	23	.027
35	+4.93	33	.027
47	+5.35	45	.022
59	+5.97	57	.023
∞	+6.73	∞	
Average			.024

II. EXPERIMENTAL

1. PREPARATION OF THE FIRST ISOMER, MANNOSE·$CaCl_2$·$4H_2O$, FROM β-d-MANNOSE

Twenty grams of β-mannose and 32 g crystallized calcium chloride dihydrate were dissolved on a boiling water bath in 28 ml of water. On standing over night at room temperature the solution crystallized to a solid mass. This was thinned out with absolute alcohol, filtered on a Büchner funnel, and washed with absolute alcohol. Dried at 35°, the yield was 28 g. It was recrystallized by slow evaporation of a concentrated aqueous solution in a desiccator. A solution of 25 g of the compound in 25 ml of cold water was filtered through an asbestos mat followed by 10 ml of water. The filtrate was placed in a crystallizing dish in a vacuum desiccator over H_2SO_4. After two weeks this solution had crystallized to a solid mass. It was triturated with absolute alcohol, filtered on a suction filter, and washed with a further quantity of alcohol. Dried at 35°, the yield was about two-thirds of the original material. It was readily soluble in water, methanol, and hot absolute alcohol. It dissolved slowly in cold 95 per cent alcohol and in acetone. It melted at 101° to 102° corr.

Analysis.—Chlorine and calcium were determined directly in an aqueous solution of the compound. Moisture was determined by drying at 50 mm over P_2O_5, first for six hours at 76°, then for 19 hours at 100°. Four hours additional drying at 110° caused no further loss in weight.

1.0197 g gave 0.8080 g AgCl, hence Cl = 19.62 per cent.
1.0239 g gave 0.1615 g CaO, hence Ca = 11.16 per cent.
Loss on drying to constant weight equaled 19.10 per cent H_2O.
Observed $[\alpha]_D^{20} = +6.72$.
Calculated for mannose·$CaCl_2$·$4H_2O$, Cl = 19.56, Ca = 11.02, H_2O = 19.80, $[\alpha]_D^{20} = +6.94$.

2. PREPARATION OF THE FIRST ISOMER, MANNOSE·$CaCl_2$·$4H_2O$, FROM VEGETABLE IVORY

A mannose sirup was prepared essentially according to the methods of Hudson and Sawyer [13] and Clark [14] though with a somewhat simplified procedure. One hundred grams of vegetable ivory meal sifted through a 48-mesh sieve was slowly added to 125 g of 85 per cent H_2SO_4 and kneaded into a thick paste. After standing at room temperature for 24 hours the paste, which had by this time become liquid, was diluted to a volume of 2 liters and boiled under a reflux condenser for three hours, or until samples which were taken at one-half hour intervals showed a constant rotation. The dark red liquor was decolorized with 20 g of active carbon and neutralized to congo red paper by slowly adding freshly precipitated, well-washed barium carbonate to the boiling solution. The precipitated barium sulphate was separated by filtration with suction and well washed. The mixed filtrate and washings were acidified with 2 ml of 5 per cent H_2SO_4, and the slight precipitate thus produced was filtered off with the addition of a further 10 g of decolorizing carbon. This colorless liquor was evaporated to a sirup of about 90 per cent solids as determined with a refractometer. To this sirup, while still warm, there was added a solution of 95 g of calcium chloride dihydrate in 60 ml of water. The mixture was stirred to a uniform solution, which was then diluted with 135 ml of equal parts of absolute alcohol and acetone. Crystallization began almost immediately after cooling and seeding. After one night at room temperature and 24 hours in an ice chest the crystals were filtered off on a Büchner funnel and washed with 400 ml of equal parts of absolute alcohol and acetone. Dried at 35° there was obtained 114 g. The melting point, analysis, and polarization data identified this product with the first isomer, mannose·$CaCl_2$·$4H_2O$, as originally obtained from crystalline β-mannose.

3. TRANSFORMATION OF THE FIRST ISOMER, MANNOSE·$CaCl_2$·$4H_2O$ INTO β-MANNOSE·$CaCl_2$·$2H_2O$

Ten grams of the first isomer was dissolved in 40 ml of hot absolute alcohol and the solution was placed on a boiling water bath. When the volume had been reduced by about one-quarter, crystals appeared.

[13] See footnote 9, p. 464.
[14] Clark, J. Biol. Chem., 51, p. 1; 1922.

By the time the volume had been further reduced to about one-half, the solution was well filled with crystals. It was then set aside at room temperature over night, filtered, and the crystals washed with absolute alcohol. Dried at 35° there was obtained 6½ g. The product was markedly different from the first isomer. The crystals were well defined, hard, triangular prisms. They were readily soluble in water and in methanol, only slightly so in cold 95 per cent alcohol, and practically insoluble in absolute alcohol. The substance melted at 159° to 160° (corr.) with decomposition.

Analysis.—Chlorine and calcium were determined directly in aqueous solution. The results agree with the percentages calculated for mannose·$CaCl_2$·$2H_2O$, but holding at 50 mm over P_2O_5 at 100° for five hours caused no loss in weight.

0.9799 g gave 0.8550 g AgCl, hence Cl = 21.59 per cent.

1.0168 g gave 0.1741 g CaO, hence Ca = 12.23 per cent.

Observed $[a]_{20}^{D} = +6.73$.

Calculated for mannose·$CaCl_2$·$2H_2O$, Cl = 21.71; Ca = 12.23; $[a]_{20}^{D} = +7.7$.[15]

4. REVERSAL OF THE ABOVE TRANSFORMATION

Ten grams of β-mannose·$CaCl_2$·$2H_2O$ was dissolved in 150 ml boiling absolute alcohol. The solution was cooled and 1.1 ml of water was added, thus sufficient to make up the deficiency between a dihydrate and a tetrahydrate. The solution was evaporated at room temperature in a current of air to a thin sirup, then seeded with crystals of the first isomer and placed in a desiccator. After a few days the sirup had crystallized to a semisolid mass. After filtering, washing with absolute alcohol, and drying at 35° there was obtained 6 g. The melting point and course of mutarotation identified it as the first isomer.

5. PREPARATION OF β-MANNOSE·$CaCl_2$·$2H_2O$ FROM β-MANNOSE OR DIRECTLY FROM VEGETABLE IVORY

This compound, though first prepared by transformation of the first isomer as described above, was subsequently obtained both from crystalline β-mannose and from hydrolyzed vegetable ivory. In the former case 20 g β-mannose with 24 g calcium chloride dihydrate was dissolved in 12 ml of hot water, the solution placed on a boiling water bath, and 80 ml of hot absolute alcohol slowly added. After remaining on the bath for one-half hour the solution was well filled with crystals. It was cooled slowly and kept at room temperature overnight. Filtered, washed with 95 per cent alcohol, and dried at 35° there was obtained 28 g.

[15] The formula, mannose·$CaCl_2$·$2H_2O$ is based upon the close agreement of the theoretical percentages of Ca and Cl with the values found. The fact that no loss of weight occurred on drying under the conditions stated does not exclude this formula. Three other compounds of this type, xylose, arabinose, and fructose calcium chlorides, also give percentages of Ca and Cl which correspond closely for hydrates, but do not lose weight on drying over P_2O_5 at 100° and 50 mm.

The same procedure of crystallizing from strong, hot alcohol was applied to the preparation of this compound directly from an impure mannose sirup. Ten grams of a thick sirup from hydrolyzed vegetable ivory prepared as described earlier was mixed with 10 g $CaCl_2 \cdot 2H_2O$, previously dissolved in 3 ml of water, on a boiling water bath. Thirty-five milliliters of warm absolute alcohol was added, and the resulting solution kept on the bath until its volume had been reduced by about one-half, when a few crystals of β-mannose$\cdot CaCl_2 \cdot 2H_2O$ were added as seed. Crystallization of the characteristic triangular prisms was soon in evidence and progressed rapidly. After a further short period on the bath and 48 hours at room temperature the crystals were separated on a Büchner funnel, washed with 95 per cent alcohol, and dried at 35°. The yield was 8½ g.

6. ACETYLATION OF β-MANNOSE$\cdot CaCl_2 \cdot 2H_2O$

Ten grams of β-mannose$\cdot CaCl_2 \cdot 2H_2O$ was added in small portions during the course of one-half hour to a mixture of 50 ml acetic anhydride and 65 ml pyridine, previously cooled in an ice bath. The mixture was held in the ice bath with frequent shaking for four hours and then kept in an ice chest for two days. When it was poured on crushed ice, crystallization of β-mannose pentaacetate took place almost immediately. The crystals were filtered on a suction funnel, washed with water, and dried at 35°. The yield of this impure material was 5½ g. The filtrate, after neutralizing with sodium bicarbonate and extracting with chloroform, gave a further 1¼ g. These two quantities of impure crystals were mixed and recrystallized from alcohol, yielding 6 g of pure β-mannose pentaacetate, or 50 per cent of the theoretical.

III. SUMMARY

Two crystalline isomeric double compounds of *d*-mannose with calcium chloride have been prepared.

One, designated the first isomer, shows an unusual course of mutarotation and an initial specific rotation which indicate that the sugar constituent of the double compound is a new form of mannose.

The extrapolated initial rotation of this compound shows a value for the mannose portion in good agreement with that previously calculated by Hudson for a β-mannose of 1, 5 ring structure.

A second isomer was obtained by evaporating an alcoholic solution of the first on a water bath. This product is a double compound of the previously known β-mannose and calcium chloride.

The preparation and study of compounds of the sugars with salts appears to offer a promising method for the discovery of new crystalline forms of the sugars.

WASHINGTON, February 13, 1929.

RP107

A STUDY OF PURIFIED WOOD FIBERS AS A PAPER-MAKING MATERIAL

By Royal H. Rasch[1]

ABSTRACT

The characteristics of purified wood fibers and commercial papers prepared from these fibers are being investigated from the standpoint of chemical purity, color, durability, and permanence and compared with other typical papers and paper-making fibers.

The interest in the purified wood fibers lies not only in their value for high-quality bond and writing papers of the grade hitherto made entirely from rag fibers or mixtures of rag and sulphite fibers but also very largely in their permanence qualities and thus the possibility of using them to supplant the higher-priced rag fibers in permanent record or other papers in which durability must be maintained over centuries.

Tests have been made on typical commercial grades of paper-making fibers, such as soda pulps, sulphite pulps, purified wood pulps, and rag half stocks. A thorough study was made of the physical properties of commercial papers made from fibers similar to the above. The effect of accelerated aging tests on the chemical and physical properties of these papers and paper-making fibers was determined in order to obtain information on the relative permanence of these materials.

The more important conclusions of this investigation follow. Accurate evaluations of the quality of papers or paper-making fibers must be based on specified performance tests. Fiber composition can not be taken as a criterion of the excellence of a paper. The manner in which the purified wood fibers and paper prepared from them react to the various tests for durability, permanence, color characteristics, etc., indicates that they are well adapted for conversion into high-quality bond and permanent record papers, which have hitherto been made exclusively from furnishes of high-grade rag half stock.

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I. PURPOSE AND SCOPE

The sulphite process of pulping wood is so recent a development in the history of paper making that, until a few years ago, very little definite information was available as to the actual aging qualities of

papers prepared from this type of cellulose fiber. It was not known how long a carefully prepared sulphite paper could resist deterioration. Observations of authentic samples of these papers, after years of natural aging, have revealed conclusively that the ordinary grades of sulphite pulps are not adaptable to the manufacture of various types of papers in which the combined qualities of great strength, durability, and permanence are required. These observations, together with the well-known fact that some century-old books printed on rag papers are still in existence in a high state of preservation, strengthened the belief that for these special qualities, particularly permanence, a paper of high-grade rag fibers was essential and that wood fibers were by nature, and as a result of drastic methods used to pulp them, relatively weak and impermanent. Supporting this belief were the early views of cellulose chemists, who held that cellulose from wood was chemically distinct from cotton cellulose. With improved methods of isolating wood cellulose in pure form has grown the belief that it is identical with cotton cellulose in its chemical properties and subject to the same reactions.

Years of research have been devoted to the purification of wood fibers for various purposes, until at the present time wood fibers for paper making are being produced commercially by special processes which make them similar in many respects to paper-making rag fibers. Owing to these similarities, the purified wood fibers are superseding the higher priced rag fibers in many papers, even in those intended for use as permanent records. No data, however, have been available to the industry on the relative merits of this new fiber and other types of paper-making fibers. In response to a general demand for information of this kind, an investigation for the purpose of obtaining such data was undertaken by the National Bureau of Standards. The purpose of this paper is to present, in the form of a progress report, the information and data which have been obtained so far on relative qualities of purified wood fibers as compared to other typical paper-making fibers.

This paper will deal with a study of the more important chemical and physical properties of papers and paper-making fibers and the effect of accelerated aging tests on these properties. The investigation has thus far been limited to a study of representative commercial products.

II. DETAILED OUTLINE OF PROGRAM

The program of work was divided into two parts—a study of paper-making fibers and a study of commercial papers. The kinds of fibers included are only those used for fine writing papers.

1. A STUDY OF PAPER-MAKING FIBERS

A preliminary study of purified wood fibers and other typical commercially prepared paper-making fibers entering into the manufacture of papers was first planned in order to determine the characteristics, principally chemical, of the different fibers and, if possible, to what extent these characteristics limit the permanence and other physical properties of papers. It was planned to obtain these samples from manufacturers of highest grade products, so that they would be representative of the best materials commercially obtainable at the present time. The following types of paper-making fibers were selected for the work, since they cover the range of fibers generally used for the manufacture of the better grades of papers:

Cotton rag half stock:[2]

From new rags.

From used rags.

Wood pulps:

Purified wood pulps.

Sulphite pulps.

Soda pulps.

Their wide variations in chemical purity and in the chemical nature of the impurities they contain offer a ready means of studying the relative effects of the different impurities on the various

[2] A brief description of the various paper-making fibers and methods used in their preparation is given below. For a more comprehensive discussion the reader is referred to the various textbooks on pulp and paper-making practice.

Most rags as they arrive at the mill require a mechanical and chemical cleaning. In the case of new white rags the constituent fibers are harsh, due to the presence of naturally occurring resins and waxes, and, even though sufficiently clean, are not well suited for direct conversion into paper. Old rags contain various impurities, such as dirt, grease, and dye, which must be removed. The rags, which are first sorted, cut into small pieces, and dusted, are boiled under pressure with lime or caustic soda or a mixture of the two. The amount of these chemicals used, as well as the other conditions of the cooking operation, vary from mill to mill and according to the kind of rags. After cooking, the rags are washed with a large volume of water in a beater and are simultaneously broken up and brushed out. The beater consists of an oval trough and a revolving beater roll on which is a series of bronze or steel blades engaging similar blades in the bottom of the trough. A means is provided for withdrawing the wash water as fast as fresh water is added. The rags are more or less discolored and require a bleaching treatment to bring them to the desired whiteness. For this purpose 1 to 5 per cent of calcium hypochlorite is used, depending upon the quality of rags. The final washed stock is technically termed "half stock" or "half stuff."

In the sulphite process wood chips are digested under pressure with a solution of bisulphites of alkaline earth metals (chiefly calcium) containing free sulphurous acid. The undesirable lignin compounds as well as a large portion of the resinous materials and sugars are broken down, while the cellulose itself remains relatively unattacked. In subsequent washing and screening operations the soluble reaction products, dirt and coarse fragments, are removed. The desired whiteness of fiber is obtained by bleaching with calcium hypochlorite and finally washing. This material is referred to as "bleached sulphite pulp."

The soda process depends upon the fact that the various undesirable impurities associated with cellulose in wood are very soluble in hot caustic soda solutions. Chips of the wood are cooked in digesters under pressure with the alkali, and the resultant fiber is washed and bleached in much the same manner as in the sulphite process. The final product is termed "bleached soda pulp."

For an idea of the methods employed in the manufacture of purified wood fibers the reader is referred to a bibliography of patents on the subject: Manufacture of High Alpha Cellulose, by Joseph Rossman, Paper Trade J., 86, No. 15, p. 206; Apr. 12, 1928; also, Production of Pulp with High Alpha Cellulose, Paper Trade J., 85, No. 8, p. 75; Aug. 25, 1927. In general, fibers of this type are prepared by digesting wood pulps, manufactured by the usual pulping processes, in alkaline media to remove the remaining undesirable noncellulosic materials, as well as any modified celluloses that were formed.

properties of the cellulose fibers with which they are associated and, consequently, of the papers into which they are converted.

It was proposed to make the commonly applied determinations, such as alpha cellulose content, copper number, pentosan content, resin content, and ash content; also, to determine the color characteristics of the fibers and their viscosity in cupra-ammonium solution. Since aging is known to have a marked effect on the chemical as well as physical properties of cellulose products, the more significant of the above tests were to be repeated on samples which had been subjected to accelerated aging tests.

2. A STUDY OF COMMERCIAL PAPERS

Next in the program of work was included a study of purified wood-fiber papers and various other types of high-grade commercial papers prepared from fibers similar to those outlined above, under 1. Included in this comparison were not only the applicable tests usually made on the paper-making fibers, but also all the commonly applied strength tests, as well as an examination of the papers for fiber composition, acidity, and for the kind and amount of sizing materials present. It was planned to make a thorough study of the probable degree of permanence of the different papers as measured by the extent to which their various chemical and physical properties resist the effects of heat, light, and moisture.

III. DESCRIPTION OF METHODS USED

1. PREPARATION OF SAMPLES

(a) PRELIMINARY TREATMENT OF WOOD PULPS AND RAG HALF STOCKS

In order to insure a high degree of uniformity in the method of handling samples, immediately upon being received they were all thoroughly mixed, slushed with water, and converted into 10 by 12 inch sheets with the laboratory hand sheet mold.[3] Sufficient stock, made into a uniform suspension with water, was taken to give sheets weighing about 40 g bone dry. The sheets were pressed between clean felts, after which they were allowed to dry at room temperature and then carefully stored for future use.

In measuring color characteristics of fibers it was found more convenient to use thinner sheets, and for this purpose sheets weighing 10 g were made up.

(b) PREPARATION OF CELLULOSE MATERIALS FOR CHEMICAL TESTING

Papers, as well as wood pulps and rag half stocks, were reduced to a fibrous form before being subjected to the various chemical tests.

[3] Shaw, M. B., and Bicking, G. W., Paper Trade J., 79, No. 21, p. 51; Nov. 20, 1924.

A discussion of the reasons for using material in this form, as well as a description of the apparatus employed, is given later on.

2. TEST METHODS

(a) CHEMICAL

(1) ALPHA CELLULOSE CONTENT.—By the so-called alpha cellulose content of a cellulosic material is meant the percentage of ash-free material resisting the action of sodium hydroxide of mercerizing strength. The method has been used to a great extent in the viscose industry as an aid to the determination of the suitability of pulps for the manufacture of rayon and to a lesser extent in the paper industry as a means of judging the chemical purity of paper-making fibers. It has become recognized that there is a relationship between the paper-making qualities of a given material and its content of caustic-resistant cellulose, and as a result more and more importance is being attached to this method. In this investigation considerable time has been devoted to this phase of the study, and a number of methods and modifications has been considered. The method as finally adopted is given below in detail.

Weigh out accurately 5 g of the air-dry disintegrated sample into a 400 ml beaker. Add 50 ml of an 18 per cent sodium hydroxide solution (1.200 specific gravity) at 20° C. Let stand one or two minutes until pulp has absorbed caustic. Macerate well with a flattened glass rod and add another 50 ml portion of caustic. Again macerate and allow to stand one-half hour from time caustic was first added, the temperature being held at 20° C. Fill the beaker with distilled water at exactly 20° C. and filter through a fine mercerized cotton cloth on a Buchner funnel. Return the filtrate through the pad of fibers and wash carefully with 1 liter of water at 20° C. Remove the filtrate and save for the beta-cellulose determination. Wash the pad with 100 ml of 20 per cent acetic acid and finally with 1 liter of boiling distilled water. Place pad in drying oven, and when fairly dry remove cloth filter, carefully scraping off with a spatula any adhering fibers. Transfer the removed fibers to a weighing bottle. Dry at 105° C. to constant weight. Report the result as per cent alpha cellulose based on bone-dry ash-free fiber. Determine the moisture and ash on a separate sample.

(2) COPPER NUMBER.—The amount of copper reduced from a Fehling's solution by a given amount of cellulose material is termed the copper number of that material. This method is in wide use as a means of measuring the reducing power of the modified or degraded celluloses and other impurities present in the fiber and is generally considered a convenient means of predicting the probable extent to which a fiber will resist chemical or physical deterioration. The

modified procedure as developed at the Bureau of Standards especially for determining the copper number of papers was used.[4]

(3) PENTOSAN CONTENT.—Together with pentosans are included any other furfural-yielding substances that may be present, such as pectins in cotton. Oxycellulose is said to give slight yields of furfural on distillation with hydrochloric acid. The method used is similar to the usual ones involving the distillation of the sample with dilute hydrochloric acid, except that precipitation was accomplished by the use of thiobarbituric acid instead of phloroglucinol.[5]

(4) RESIN CONTENT.—The resin content as determined includes all the substances present which are extractable with acidulated alcohol, such as rosin used in sizing papers, naturally occurring resins, waxes, etc. The official procedure [6] of the Technical Association of the Pulp and Paper Industry was followed.

(5) ASH CONTENT.—The ash content is of importance, since it indicates the amounts of mineral residues left in the fibers and, in the case of papers, whether a mineral filler has been added. The official T. A. P. P. I. procedure was followed.

(6) ACIDITY.—Acidity in paper is usually due to one or both of two causes—either to alum (which is added to the beater as a precipitant in rosin sizing and to the glue as a preservative for surface sizing) or to the acidic nature of decomposition products of cellulose itself. This decomposition, resulting in the development of acidity, is thought to be due to auto-oxidation resulting from the presence of alum or other inorganic acid materials or from the use of paper-making fibers containing oxycelluloses, lignin, or other impurities which affect their stability. Therefore, in any study of permanence, acidity is a factor of extreme importance. The method described by Hall has been tentatively adopted.[7] Acidity number may be described as the number of cubic centimeters of 0.01 normal sodium hydroxide solution required to make the extract of 10 g of bone-dry disintegrated fiber neutral to phenolphthalein indicator.

(7) GLUE.—The amount of glue used in surface-sized papers has a marked effect upon many of the strength qualities of the papers. The official T. A. P. P. I. method was used.

(b) PHYSICAL

(1) COMMONLY APPLIED TESTS.—All the commonly applied, official T. A. P. P. I. paper-testing methods were used—as basis weight, thickness, bursting strength, folding endurance, tearing strength, and tensile strength.

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[4] Scribner, B. W., and Brode, W. R., A Modified Method for the Determination of the Copper Number of Paper, B. S. Tech. Paper No. 354; Sept. 24, 1927. Price, 5 cents. Superintendent of Documents, Washington, D. C.

[5] Directions given by Dox and Plaisance, J. Am. Chem. Soc., **38**, p. 2156; 1916.

[6] Copies of the official paper-testing methods of the Technical Association of the Pulp and Paper Industry may be obtained from the secretary at 18 East Forty-first Street, New York, N. Y.

[7] Kohler, S., and Hall, G., Acidity in Paper, Paper Industry, **7**, No. 7, pp. 1–5; October, 1925.

(2) COLOR.—In classifying various papers and paper-making fibers according to their color characteristics, or, more especially, in comparing the stability of samples of these materials toward accelerated aging tests, ordinary methods of grading according to observations of the unaided eye are unsuited, since the variations are in many cases extremely slight. In this investigation, comparisons of color characteristics were based on measurements made with the Pfund colorimeter.[8]

(c) ACCELERATED AGING TEST

(1) EXPOSURE TO DRY AIR AT 100° C.—The exposure of samples being investigated for permanence qualities to elevated temperatures offers the most convenient of the available methods. This is one of the methods used at the Government Testing Institute at Stockholm in its investigation of permanence of papers and was considered by the workers there to closely simulate the effects of natural aging.[9] As this test was conducted at the Bureau of Standards, a closed oven of the electric resistance type was employed. (See fig. 1.) A fan and air duct keep the air in constant, rapid circulation, thus maintaining a uniform temperature throughout the oven. A thermostat and relays were provided for controlling the temperature. The variations in temperature in an oven of this type are within ±1° C. Suitable racks are provided for suspending the samples.

(2) EXPOSURE TO HUMIDIFIED AIR AT 95° C.—This test was used to study the combined effects of heat and moisture on the various characteristics of papers. The test was conducted in the same oven described under (1). Beakers of water were placed in the oven in order to humidify the atmosphere.

(3) EXPOSURE TO RAYS FROM ARC LIGHT.—A study in the chemistry division of the Bureau of Standards of apparatus designed for finding the effect of light on materials has revealed the fact that a carbon arc lamp is well adapted to simulate the effects of natural sunlight and to give reproducible results when the conditions under which the samples are maintained during exposure are carefully controlled. For this purpose a cabinet has been provided in which the temperature and humidity may be kept at any desired point. (See figs. 2 and 3.) Top and sides (except exposure side) consist of triplicate window glass, while the exposure side consists of two thicknesses of a special glass, which is thinner and is said to be somewhat more transparent to the rays from the arc than is ordinary glass. A thermostat was provided for controlling the temperature, and a small fan keeps the air circulated and uniform in temperature

[8] Pfund, A. H., A New Colorimeter for White Pigments and Some Results Obtained by Its Use, Am. Soc. for Testing Materials; June, 1920; also Lofton, R. E., A Measure of the Color Characteristics of White Papers, B. S. Tech. Paper No. 244; Aug. 28, 1923. Price, 5 cents, Superintendent of Documents, Washington, D. C.

[9] Hall, G., Permanence of Paper, Paper Trade J., **82**, No. 14, pp. 185–191; Apr. 8, 1926

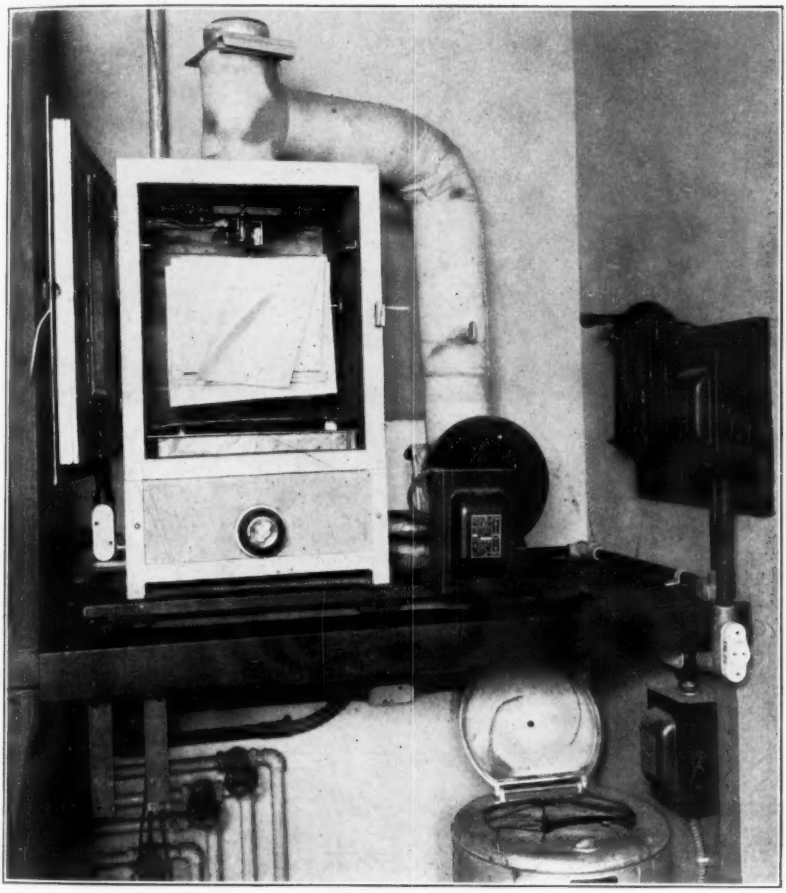

FIGURE 1.—*Oven used for accelerated aging test*

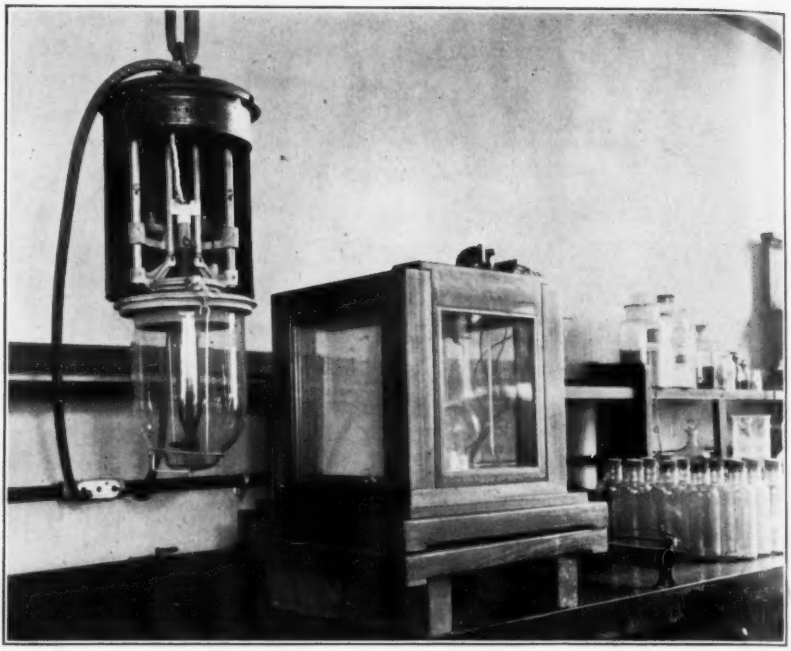

FIGURE 2.—*Carbon-arc lamp and air-conditioning cabinet*

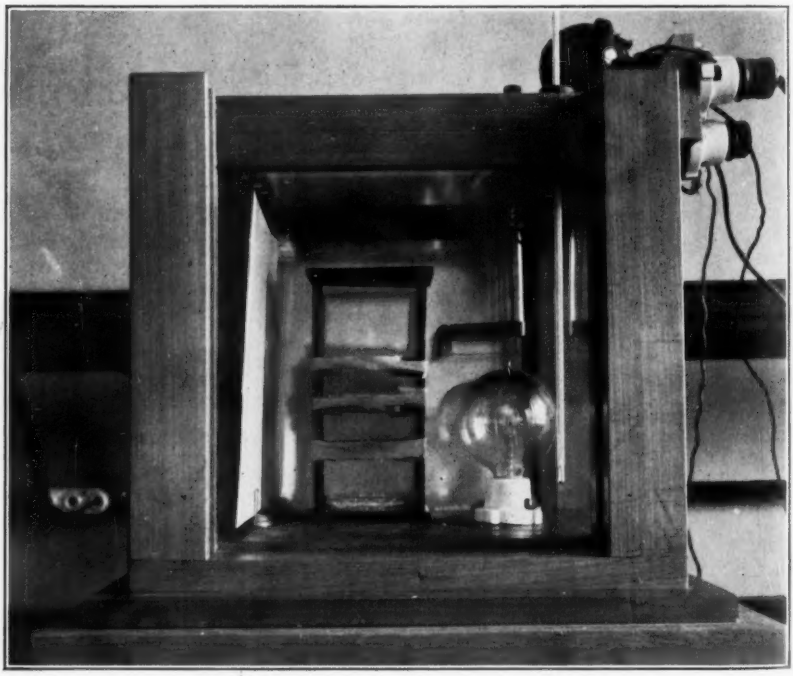

FIGURE 3.—*Air-conditioning cabinet*

throughout the cabinet. The desired humidity is maintained by means of a saturated solution of the proper salt.

(4) Exposure to Steam at Atmospheric Pressure.—The use of steam as an accelerated aging test is based upon the observation that papers or pulp samples when exposed to the action of live steam show a marked tendency to revert in color. This test was conducted in a galvanized-iron chest well insulated with magnesia and provided with a cover containing a number of holes to permit the escape of steam. Live steam was injected through an inlet in the bottom of the chest. The samples to be exposed were suspended on suitable racks provided in the cabinet.

IV. DESCRIPTION OF SAMPLES STUDIED

Following are tabulations of the samples studied, together with their code numbers and a brief description of each sample as given by the manufacturer who supplied it.

1. PAPER-MAKING FIBERS

The following samples of paper-making fibers represent products of 13 different manufacturers:

No.

1. Bleached sulphite pulp. Bond-paper grade.
2. } Purified wood pulp. Paper-making grade.
3. }
4. Bleached soda pulp. Book-paper grade.
5. Old colored rag half stock. "Twos and blues" grade.
6. New white rag half stock. "No. 1 unbleached" grade.
7. Bleached sulphite pulp Bond-paper grade.
8. Old white rag half stock. "No. 1 white" grade.
9. New white rag half stock. "New white shirt cuttings."
10. Old white rag half stock. "Extra No. 1 white" grade.
11. New white rag half stock. "Unbleached muslins."
12. New white rag half stock. "Mixture of 75 per cent new white shirt cuttings and 25 per cent bleached shoe cuttings."
13. Old white rag half stock. "Mixture of 50 per cent No. 1 white and 50 per cent No. 2 white cottons."
14. New white rag half stock. "New white shirt cuttings."
15. New colored rag half stock.
16. Old white rag half stock. "Old white cuttings."
17. Bleached sulphite pulp. Bond-paper grade.
18. Purified wood pulp. Special grade for esterification.
19. } Bleached sulphite pulp. Special grade for esterification.
20. }
21. } Bleached soda pulp. Book-paper grade.
22. }
23. }
24. } Bleached sulphite pulp. Bond-paper grade.
25. }
26. } Purified wood pulp. Paper-making grade.
27. }

28. Purified wood pulp. Special grade for esterification.
29.
30.
31. Purified wood pulp. Paper-making grade.
32.

2. COMMERCIAL PAPERS

The following papers represent products of 12 different manufacturers:

No.
101. All-rag bond paper. Prepared from new rags; rosin [10] and glue sized.[11]
102. All-rag bond paper. Prepared from new rags; rosin and glue sized.
103. Rag paper. Prepared from new rags. Contains a small amount of sulphite fiber; rosin and glue sized.
104.
105.
106. Purified wood fiber paper; rosin and glue sized.
107.
108. Sulphite writing paper; rosin sized.
109.
110. Sulphite bond paper; rosin sized.
111. Bond paper prepared from a mixture of rag fiber and sulphite pulp; rosin sized.
112. Same paper as No. 111, but surface sized with glue.
113. All-rag bond paper. Prepared from new rags; rosin and glue sized.
114. All-rag bond paper. Prepared from new rags; rosin sized.
115.
116. Sulphite bond paper. Rosin sized.
117.
118. All-rag bond paper. Same as No. 114, but surface sized with glue.
119. All-rag bond paper. Prepared from new rags; rosin sized.
120. All-rag bond paper. Same as No. 119, but surface sized with glue.
121. All-rag waterleaf [12] paper. Used for acetylation.
122. Purified wood-fiber paper. A waterleaf paper used for nitration.
123. Book paper. The beater furnish was 50 per cent soda pulp, 25 per cent sulphite pulp, and 25 per cent converted old papers; high clay content; rosin sized; high finish.
124. Book paper. Beater furnish similar to No. 123, but has lower clay content; bulkier and softer sheet than No. 123.
126. All-rag bond paper. Prepared from 60 per cent new white shirt cuttings and 40 per cent unbleached muslins; rosin and glue sized.
127. The same paper as No. 126 sampled before the glue-size tub.

---

[10] Ordinary printing and book papers and sulphite bond papers are sized with rosin alone. This operation takes place in the beater. A suspension of free rosin in a solution of sodium resinate is added to the stock in the beater, and after it has been thoroughly incorporated with the fiber, aluminum sulphate is added to set the sizing material. The subsequent drying on the finishing end of the paper machine fuses the rosin particles and completes the efficiency of the sizing operation.

[11] High-grade bond and record papers are "tub sized" or "surface sized" with glue. Glue imparts to papers many desirable qualities impossible to obtain by the use of rosin size alone; for example, an excellent writing surface, increased durability and resistance to wear, as well as certain intangible qualities of appearance, feel, etc. Papers of this type are practically always first rosin sized in the usual manner and then surface sized by passing the sheet through a solution of animal glue. In the best practice the glue-treated paper is loft dried; that is, it is suspended in a festoon arrangement in a special chamber where it is dried under carefully controlled conditions of temperature and humidity.

[12] "Waterleaf" is a mill term signifying unsized paper. Such paper is usually of a very absorbent nature and unsuited for writing on or purposes where a degree of water resistance is required.

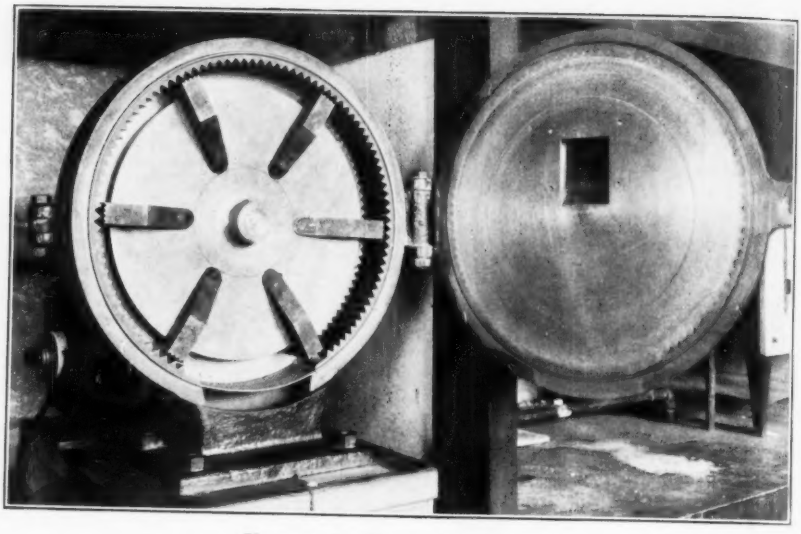

FIGURE 4.—*Paper disintegrator*

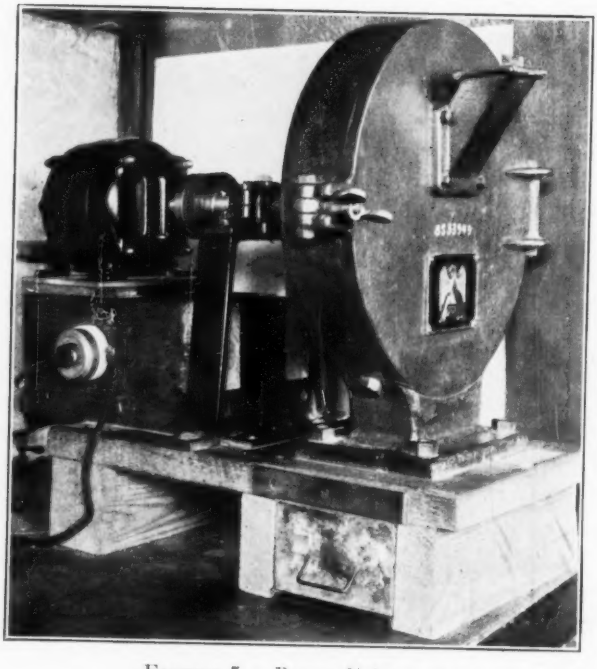

FIGURE 5.—*Paper disintegrator*

128. All-rag bond paper. Prepared from 100 per cent unbleached muslins; rosin and glue sized.
129. The same paper as No. 128 sampled before the glue-size tub.
130. All-rag paper. Prepared from 100 per cent "No. 1 white old rags"; rosin and glue sized.
131. The same paper as No. 130 sampled before the glue-size tub.
132. Paper prepared from a mixture of rag fiber and sulphite pulp Rosin and glue sized.
133. The same paper as No. 132 sampled before the glue-size tub.
134. Sulphite bond paper. Rosin sized.
135. Sulphite writing paper. Rosin sized.
147. Book paper, magazine grade. The beater furnish for this paper was 87 per cent soda pulp and 13 per cent sulphite pulp; high clay content; rosin sized.
148. Coating paper.[13] The beater furnish [14] for this paper was 24 per cent sulphite pulp, 62 per cent purified wood fiber, and 14 per cent broke,[15] low clay content; rosin sized.
152. Book paper. Rosin sized. The beater furnish for this paper was 70 per cent soda pulp and 30 per cent sulphite pulp; high clay content; rosin sized.

V. RESULTS

1. WOOD PULPS AND RAG HALF STOCKS

(a) CHEMICAL CHARACTERISTICS AND REACTION TOWARD ACCELERATED AGING TESTS

(1) Alpha Cellulose Content.—Most procedures for the determination of alpha cellulose specify that the material being tested, especially if it is a wood pulp, shall be in the form of squares of a given size and thickness. Ordinarily this procedure is quite satisfactory, but for the purposes of the present investigation it has been considered advisable to make this and other chemical tests, such as copper number and acidity, with material disintegrated in a special apparatus provided for that purpose.[16] (See figs. 4 and 5.) It is very difficult to macerate papers, particularly sized and highly finished papers, with mercerizing caustic solution, and impossible to do so in a reproducible manner (even with waterleaf papers) unless the sizing material and formation of the sheet is broken up in such a way as to make the fibers available to the action of the caustic. The least objectionable method of accomplishing this result appears to be by the use of the disintegrator already referred to. In order to establish uniform methods of procedure in this work and to have a common basis for the comparison of alpha cellulose values obtained on papers and on paper-making fibers, it was considered desirable to convert the latter

[13] Coating papers are those used as a base for enameled or coated papers.
[14] This paper was found to contain 25 per cent deciduous wood fiber.
[15] "Broke" is the trimmings and waste from the paper machine.
[16] Hall, G., Permanence of Paper, Paper Trade J., 82, No. 14; pp. 185-191; Apr. 8, 1926; also, Scribner, B. W., and Brode, W R., A Modified Method for the Determination of the Copper Number of Paper, B. S. Tech. Paper No. 354; Sept. 24, 1927. Price, 5 cents, Superintendent of Documents, Washington, D. C.

into the same disintegrated form before applying the alpha cellulose and other chemical tests. In obtaining comparative alpha cellulose values for different types of fibers there is another factor that requires consideration. Different materials in sheet form do not macerate with equal ease in mercerizing caustic, although this would appear to be essential where a direct comparison of this type is being made. For example, it was found that squares of purified wood fibers absorbed the caustic readily, forming a smooth, even suspension of well-separated fibers, thus exposing a maximum of surface to the action of the caustic; on the other hand, the rag half stocks, more or less in the form of small bits of cloth, threads, and knots, could not be thoroughly pulped at all. Another difficulty encountered was that the soda pulps became extremely resistant to the penetration of caustic after the heat treatment. It was found, however, that all the above difficulties could be obviated by using disintegrated fiber. Table 1 summarizes the effects of grinding on different types of materials. Each value is a composite of results obtained on all available samples of a given type of material. It is clear that the alpha cellulose values obtained on disintegrated fibers are from 1 to 2 per cent lower than those obtained on materials in sheet form, and that this decrease is somewhat greater for rag half stocks than for wood pulps.

TABLE 1.—*Effect of disintegration on alpha cellulose content of typical paper-making fibers*

Type of fiber	Alpha cellulose content		Difference in alpha cellulose content caused by disintegration
	One-fourth inch squares of sheeted fibers	Disintegrated fibers	
	Per cent	*Per cent*	
New rag	99.0	97.0	2.0
Used rag	95.5	93.4	2.1
Purified wood fiber	94.0	92.6	1.4
Sulphite pulp	85.8	84.5	1.3
Soda pulp	75.1	73.9	1.2

In Table 2 the alpha cellulose results obtained for individual samples of paper-making fibers are given, also results obtained with samples heated 72 hours at 100° C. The effect of this artificial aging is expressed as the percentage of original alpha cellulose lost.

TABLE 2.—*Chemical tests on various paper-making fibers*

Sample No.	Alpha cellulose content			Copper number			Resin (control sample)	Pentosans (control sample)	Ash (control sample)
	Control sample	Sample heated 72 hours at 100° C.	Amount of initial alpha cellulose lost	Control sample	Sample heated 72 hours at 100° C.	Increase in copper number			
	Per cent	*Per cent*	*Per cent*			*Per cent*	*Per cent*	*Per cent*	*Per cent*
TESTS ON RAG HALF STOCKS									
11	98.2	98.1	0.1	0.79	1.00	27	0.29		0.21
9	97.7	97.7	.0	.77	.89	16	.33	0.23	.16
12	97.5	97.0	.5	.77	.89	16	.28		.10
6	96.7	96.3	.4	.82	.97	18	.40	.13	.14
16	95.8	95.3	.5	1.26	1.35	7	.28		.10
14	95.1	94.3	.8	1.24	1.41	14	.30		.16
8	94.2	93.2	1.1	1.05	1.14	9	.94	.12	.28
15	93.5	92.3	1.3	1.82	1.94	7	.37		.41
13	92.1	91.1	1.2				.72		.24
10	91.4	90.3	1.2	.93	1.33	43	.67		.24
5	83.8	81.6	2.6	2.55	2.80	10	.79	.33	.50
TESTS ON PURIFIED WOOD PULPS									
3	93.8	93.6	0.2				0.29	2.12	0.15
27	93.2	93.3	[1].1	1.33	1.44	8	.20		.10
18	93.2	92.7	.5				.32		.12
28	93.1	92.8	.3				.31		.14
2	92.4	92.5	[1].1				.27	3.32	.19
31	92.4	92.2	.2	.89	1.00	12	.32		.09
26	92.3	92.5	[1].2	1.23	1.34	9	.38		.13
32	91.9	91.9	.0	.90	.98	9			.10
29	91.5	91.2	.3	.89	1.02	14	.25		.19
30	91.5	91.3	.2	.93	1.06	14	.27		.19
TESTS ON SULPHITE PULPS									
20	86.5	85.1	1.6				0.77		0.22
19	86.1	85.3	.9				.81		.16
17	85.3			3.22	3.18	1	.49		.19
23	84.8	83.2	1.9	3.20	3.25	2	.63		.15
7	84.1	83.0	1.3	3.32	3.55	7	.10	3.86	.16
25	83.8	82.7	1.3				.72		.14
24	83.2	81.9	1.6	2.98	3.10	4	.50		.17
1	82.7	81.3	1.7	3.29	3.45	5	.52	3.32	.23
TESTS ON SODA PULPS									
21	78.9	78.5	0.5	2.54	2.58	2	0.72		0.58
4	74.6	73.5	1.5	3.71	4.01	8	.89	12.12	.32
22	68.1	66.0	3.1	2.57	2.96	15	.45		.52

[1] Gain.

Although several different types of rag half stocks, widely different in their various properties, are included in this study, it is convenient to consider them together in one group. New, carefully bleached cotton cloth has an alpha cellulose content of very nearly 100 per cent; that is, it is practically pure cellulose. Therefore, the values obtained for the half stocks represent the extent to which the cellulose has been modified or degraded either in preliminary treatments or in the actual preparation of the half stock. New, white, unused rags require a

much less drastic treatment in their preparation than colored or used rags, and therefore may be expected to have a much higher percentage of unchanged cellulose. The results reveal this to be the case. The half stocks prepared from new white shirt cuttings, unbleached muslins, and the like have alpha cellulose values ranging from 95.1 to 98.2 per cent; a half stock prepared from new colored rags (No. 15) had a value of 93.5 per cent; half stocks from good grades of old white rags contained from 91.4 to 95.8 per cent of alpha cellulose. The grade known as "twos and blues" (No. 5), one sample of which was available for study, is prepared from old colored rags which require very drastic cooking and bleaching treatments in order to convert them into paper-making half stock. Its alpha cellulose content is evidently a fairly accurate indication of how drastic this treatment has been.

It is evident from a glance at the column of results indicating the loss in alpha cellulose suffered by the various half stocks due to the heat treatment that the stability of these samples is dependent mainly upon the original alpha cellulose content. These results with half stocks lend themselves to interpretation more readily than those obtained with wood fibers because the caustic-soluble impurities present are of a less complex nature, consisting almost entirely of modified celluloses. These degradation products of the pure cellulose probably aid catalytically, in proportion to the amounts present and their chemical nature, to cause further oxidation of the remaining cellulose. The heat probably accelerates an oxidizing action, which, under normal aging conditions would take years. As the half stocks studied have a wide range of chemical purities, similarly do they present examples of great variations in stability toward artificial aging. New rag half stocks—that is, those of highest grade—are, in general, very stable to the effects of the heat treatment. It appears, however, that this is not necessarily the case, for sample No. 14, although prepared from new white rags, has an alpha cellulose content of but 95.1 per cent (low for this type of material) and is correspondingly less stable than others of this type. On the other hand, sample No. 16 gives evidences of having been carefully processed, since, although prepared from a grade of used rags, it has an alpha cellulose content of 95.8 per cent and loses but 0.5 per cent of this on being heated. To further illustrate the effects of oxycelluloses on the permanence qualities of cellulose fibers, samples of high-grade rag half stock were purposely overbleached with different amounts of calcium hypochlorite. The bleached samples were thoroughly washed to remove chemical residues, made into sheets on the laboratory hand mold, and then allowed to dry at room temperature. Alpha cellulose determinations were made on the original and the heat-treated samples. These values, which are given in Table 3, indicate very clearly the damaging influence of oxycellulose

on the stability of cellulose fibers. They further serve to show the importance of the alpha cellulose determination.

TABLE 3.—*Effect of oxycellulose in overbleached rag half stock on permanence of alpha cellulose*

Bleach consumed	Alpha cellulose content		Decrease in initial alpha cellulose content
	Before heating	After heating 72 hours at 100° C.	
Per cent	*Per cent*	*Per cent*	*Per cent*
0	98.2	98.1	0.1
1	95.5	94.4	1.2
3	87.3	85.4	2.2

It might be predicted that the wood fibers would react differently toward the accelerated aging tests than the rag fibers, since they contain impurities not present in the latter in any appreciable amounts. It could be reasonably assumed, for example, that the pentosans, which are present in wood fibers and almost entirely absent from rag fibers, would have a different effect on the stability of cellulose than would the oxycelluloses. Also, wood pulps contain some gamma cellulose (the caustic-soluble portion of a cellulose, which, in contradistinction to beta cellulose, is not precipitated by acid), which was found to be almost entirely absent in any of the various types of rag stocks. Lignins which occur in wood are probably not present in sufficient amounts, however, in any of the fibers here studied to influence the results obtained. In addition to the impurities distinct in nature from those present in rags, wood fibers also contain modified celluloses formed during the cooking and bleaching operations. It is not known how the modified celluloses in different types of wood fibers resemble in their chemical characteristics one another or those found in rag half stocks, but it appears that, regardless of source, they are exceedingly detrimental to the permanence of the fiber.

To determine the precise effect of the different impurities found in wood pulps on such qualities as permanence and to assign definite weights to them is obviously impossible except in an indirect way. It is possible, however, to study the combined effect of these impurities on the stability of the cellulose fibers with which they are associated. The purified wood fibers are all very stable in alpha cellulose content to a 72-hour heating at 100° C., equaling in this respect the highest grade rag half stock, despite the fact that they are on the average about 4 per cent lower in initial alpha cellulose content. They are distinctly superior to used white rag half stocks, although the alpha cellulose contents of the two materials are about the same. It will be further observed that sample No. 5 (a half stock prepared from used colored rags), although it has an alpha cellulose content within the range of those of the ordinary sulphite

wood pulps studied, is much less stable than they are. Again, soda pulps are seen to be exceedingly resistant to the artificial aging test, considering the large amount of caustic-soluble material they contain. Referring to Figure 6, in which the relationship between original alpha cellulose content and percentage loss resulting from 72-hour heat treatment at 100° C. is expressed graphically, it appears that the position of the curves for different types of fibers is determined by the character of the caustic-soluble constituents of these fibers. Apparently, a soda pulp having an alpha cellulose content of about 82 per cent would equal in stability a purified wood fiber of 94 per cent or a rag fiber of 98 per cent. This could be explained by assuming that the caustic-soluble impurities in wood pulps are, weight for weight, more passive in their deteriorating effects upon cellulose than those found in rag half stocks.

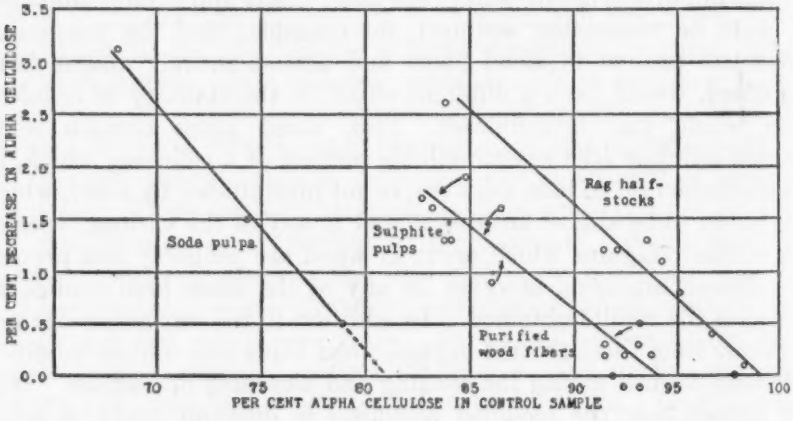

FIGURE 6

(2) COPPER NUMBER.—The copper numbers obtained for the various paper-making fibers are given in Table 2, together with the values for heat-treated samples. The copper numbers of the new white rag half stocks range from 0.77 to 1.24 and appear to be slightly lower, on the average, than the copper numbers obtained on purified wood fibers, which range from 0.89 to 1.33. Other grades of rag half stock range in values from 0.93 to 2.55. The ordinary types of wood fibers have considerably higher copper numbers than either the purified wood fibers or the better grades of half stock. In general, the lower the alpha cellulose content of fibers the higher will be its copper number. There are marked exceptions to this, however, the most striking being the soda pulps, which have a much lower alpha cellulose content than sulphite pulps; and yet they have in most cases lower copper numbers.

The increase in copper number after heating appears to offer no clue as to the probable relative permanence of the different types of

fibers. In some cases the change apparently caused by the heating is within the range of experimental error, and therefore no great significance can be attached to the results.

(3) PENTOSANS.[17]—Only a limited number of pentosan values are given in Table 2; however, these values are probably representative of those which would be obtained on other materials of a given type of paper-making fiber. The rag half stocks here studied, contain extremely small, almost negligible, amounts of furfural-yielding substances, whereas all the wood fibers contain appreciable quantities. The purified wood fibers contain from 2 to more than 3 per cent, the ordinary sulphite wood pulp from over 3 to nearly 4 per cent, while the one sample of soda pulp tested had pentosans to the amount of 12 per cent. The fact that soda pulps do contain such large amounts of pentosans, and still have relatively good permanence qualities as compared to ordinary grades of sulphite pulps or poorer grades of rag half stock, suggests that these substances do not contribute to the deterioration of cellulose to nearly the extent that the modified celluloses do. The pentosan content of the purified wood fibers may also account for the fact that these fibers, approximately 4 per cent lower in alpha cellulose content than high-grade rag half stocks, are so comparatively stable toward the accelerated aging test; that is, a great part of the difference in the alpha cellulose contents of the two materials represents this content of relatively inert pentosans.

It was previously noted that soda pulps had lower copper numbers than the sulphite pulps, which are characterized by a higher alpha cellulose content. This is undoubtedly due to the fact that the pentosans, which are known to have no aldehyde groupings and consequently no reducing power toward Fehling's solution, are present in the former to a much greater extent.

(4) OTHER TESTS.—The resin contents (alcohol-extractable materials) of the various fibers are given in Table 2. This impurity is present to a slight, and about the same, extent in new white rag half stock and in the purified wood fibers. In ordinary wood pulps and in the used grades of rag half stocks it is usually present in much greater amounts.

The ash contents of the various samples are also given in Table 2. With the exception of the soda pulps and a few of the poorest half stocks, these values are low and of little significance.

(b) PHYSICAL CHARACTERISTICS AND REACTION TOWARD ACCELERATED AGING TESTS

(1) COLOR CHARACTERISTICS.—High whiteness and brilliance are usually desired qualities in fine papers, as is also the ability of the papers to preserve these qualities over long periods of time. The

[17] Determinations made by K. S. Markley, associate chemist, Bureau of Standards.

whiteness of fibers is often a direct indication of its chemical purity. The impurities generally indicated by poor color are the various natural coloring matters—resins, gums, lignin, etc. Cellulose fibers may, however, contain large quantities of oxycelluloses and yet have a highly brilliant color.

In order to obtain information on the color characteristics of the various paper-making fibers and likewise on the relative permanence of these qualities, sheets of the different samples were tested on the Pfund colorimeter and the color characteristics compared with those obtained on similar sheets heated for 72 hours at 100° C. Colors were determined in terms of relative brightnesses for three different wave lengths of light (red, green, and blue). The values obtained are given in Table 4.

TABLE 4.—*Color stability of various paper-making fibers*

Sample No.	Brightness value of control sample				Brightness value of sample heated at 100° C. for 72 hours				Decrease in brightness values due to heating				Remarks
	Blue	Green	Red	Total brightness [1]	Blue	Green	Red	Total brightness [1]	Blue	Green	Red	Total decrease [2]	
RAG HALF STOCKS													
11	0.84	0.89	0.92	0.88	0.82	0.88	0.92	0.87	0.02	0.01	0.00	0.010	New white rags.
9	.84	.89	.92	.88	.82	.88	.92	.87	.02	.01	.00	.010	
12	.84	.90	.93	.89	.82	.88	.93	.88	.02	.02	.00	.013	
6	.83	.88	.92	.88	.80	.87	.91	.86	.03	.01	.01	.017	
14	.83	.90	.92	.88	.78	.88	.92	.86	.05	.02	.00	.023	
16	.84	.90	.93	.89	.80	.88	.93	.87	.04	.02	.00	.020	Old white rags.
8	.80	.87	.91	.86	.78	.87	.91	.85	.02	.00	.00	.007	
13	.80	.88	.92	.87	.76	.86	.92	.85	.04	.02	.00	.020	
10	.79	.88	.93	.87	.77	.87	.92	.85	.02	.01	.01	.013	
15	.72	.82	.86	.80	.70	.81	.85	.79	.02	.01	.01	.013	New colored rags.
5	.72	.82	.87	.80	.68	.79	.86	.78	.04	.03	.01	.027	"Two's and blues."
PURIFIED WOOD PULPS													
27	0.87	0.93	0.93	0.91	0.84	0.93	0.93	0.90	0.03	0.00	0.00	0.010	
18	.80	.90	.92	.87	.76	.88	.93	.86	.04	.02	.00	.020	
28	.86	.93	.93	.91	.84	.93	.93	.90	.02	.00	.00	.007	
31	.87	.93	.93	.91	.83	.91	.93	.89	.04	.02	.00	.020	
26	.86	.93	.93	.91	.84	.93	.93	.90	.02	.00	.00	.007	
29	.85	.93	.92	.90	.82	.90	.93	.88	.03	.03	.00	.020	
30	.86	.93	.92	.90	.82	.91	.93	.89	.04	.02	.00	.020	
SULPHITE PULPS													
20	0.78	0.90	0.93	0.87	0.71	0.86	0.92	0.83	0.07	0.04	0.01	0.040	
19	.77	.89	.92	.86	.74	.86	.92	.84	.03	.03	.00	.020	
17	.77	.87	.93	.86	.73	.85	.91	.83	.04	.02	.02	.027	
23	.72	.85	.90	.82	.68	.81	.88	.79	.04	.04	.02	.033	
7	.73	.85	.91	.83	.65	.79	.88	.77	.08	.06	.03	.057	
25	.77	.86	.90	.84	.71	.84	.90	.82	.06	.02	.00	.027	
24	.74	.85	.90	.83	.70	.83	.90	.81	.04	.02	.00	.020	
SODA PULPS													
21	0.66	0.81	0.89	0.79	0.62	0.77	0.88	0.76	0.04	0.04	0.01	0.030	
4	.70	.81	.89	.80	.65	.78	.88	.77	.05	.03	.01	.030	
22	.67	.80	.89	.79	.64	.78	.88	.77	.03	.02	.01	.020	

[1] Approximate brightness for white light. [2] Decrease in approximate brightness for white light.

The higher and the more uniform the reflection coefficients for a given material are the closer does it approach a true white color. Pfund [18] states: "* * * if it reflects nonselectively it is to be called 'white.' According to this nomenclature, true grays are whites of different brightness." It will be seen that all the samples are inclined toward the yellow; that is, they are deficient in the blue reading. The new white rag half stocks and purified wood fibers, with the exception of No. 18, are examples of relatively good whites; on the other hand, the soda pulps are poor in color, since the values for the reflection coefficients diverge considerably and they are relatively low on the brightness scale. An approximate indication of the total brightness of the samples—that is, brightness for white light—is obtained by arbitrarily averaging the reflection coefficients for red, green, and blue.[19] The color characteristics of the various samples of a particular group of paper-making fibers seem to be fairly typical for that particular group. For convenience these results have been composited and are expressed graphically in Figure 7. The curves approaching closest to a horizontal position represent the samples which are best in respect to nonselective reflection and thus the best whites. Relative brightnesses are indicated by the positions of the curves on the vertical scale. Color reversion, or the decrease in brightness, caused by accelerated aging, is represented in very nearly the correct proportion on the diagram by the distance between the green values for the original and for the heated sample.

Wood fibers prepared by the ordinary pulping processes (that is, sulphite and soda pulps) are much more seriously affected by the heat treatment than either the rag half stocks or purified wood fibers. The used white rag half stocks of high grade, although of a somewhat poorer initial color than half stocks prepared from new rags, do not appear to revert in color to any greater extent than the latter do. Purified wood fibers as well as high-grade rag fibers apparently retain their excellent initial color characteristics after the heating. Soda pulps appear to be somewhat more stable than the ordinary sulphite pulps in this respect.

(2) Microexamination of Heat-Treated Fibers.[20]—It was thought that the degradation of the color and other properties of cellulose fibers might be indicative of the physical breaking of the individual fibers, and that some evidence of the change in physical structure might be obtained by examining the fibers microscopically before and after the 72-hour period of high-temperature treatment.

[18] Pfund, A. H., A New Colorimeter for White Pigments and Some Results Obtained by Its Use, Am. Soc. Test. Materials, June, 1920.

[19] In order to determine the true brightness for white light, readings would either have to be taken without the colored glasses or proper factors would have to be applied to the red, green, and blue readings before they were averaged. The excitation value for blue is small as compared to green and red.

[20] Examinations made by R. E. Lofton, associate physicist, Bureau of Standards.

Accordingly, slides of typical fibers, both original and heated, were made up and examined at magnifications of 100, 200, 400, and 800 diameters. No difference, however, appeared between the untreated and the heat-treated fibers in any case. The fibers remained as

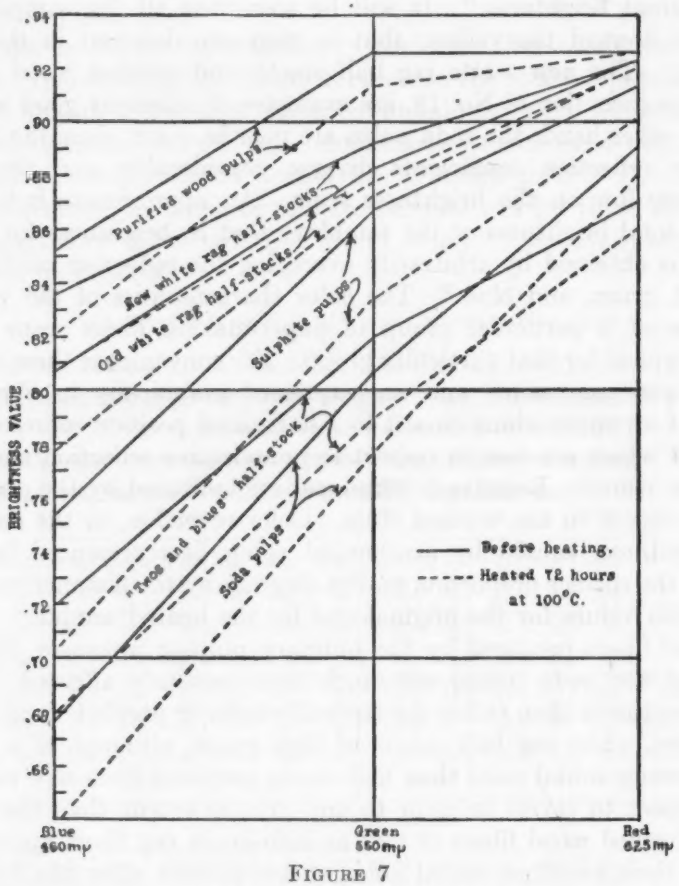

FIGURE 7

unbroken after treatment as they were originally, and no structure changes could be observed.

2. PAPERS

(a) DURABILITY AND PERMANENCE CHARACTERISTICS

(1) GENERAL CONSIDERATION OF STRENGTH TESTS APPLIED TO PAPERS.—All the commonly applied strength tests were made on original and artificially aged papers in order to compare their relative qualities of durability and permanence; that is, folding endurance, tearing strength, bursting strength, and tensile strength. The results obtained on each of the papers are given in Table 5.

TABLE 5.—*Test data on various artificially aged papers*

TESTS ON ALL-RAG PAPERS

Sample No.	Fiber composition: Rag	Fiber composition: Coniferous wood	Fiber composition: Deciduous wood	Kind of sizing used	Chemical tests: Glue	Chemical tests: Resin	Ash	Aging test: Temperature	Aging test: Duration	Weight, 500 sheets 25 by 40 inches	Thickness	Bursting strength	Ratio bursting strength to weight	Folding endurance: Machine direction	Folding endurance: Cross direction	Folding endurance: Average	Folding endurance in per cent of initial: Machine direction	Folding endurance in per cent of initial: Cross direction	Folding endurance in per cent of initial: Average	Tearing strength: Machine direction	Tearing strength: Cross direction	Tearing strength: Average	Tensile strength: Machine direction	Tensile strength: Cross direction	Tensile strength: Average
	Per cent	*Per cent*	*Per cent*		*Per cent*	*Per cent*	*Per cent*	*° C.*	*Hours*	*Pounds*	*Inch*	*Points*[1]	*Per cent*	*Double folds*	*Double folds*	*Double folds*	*Per cent*	*Per cent*	*Per cent*	*g*	*g*	*g*	*kg*	*kg*	*kg*
101-0	100	0	0	Rosin and glue-sizing.	8.89	2.8	1.51	(2)		75.6	0.0048	91	120	3,525	2,490	3,008				129.2	102.8	116.0	14.4	9.6	12.0
101-H24								100	24			88	116	2,400	1,825	2,113	68.1	73.3	70.7	125.2	101.6	113.4	13.6	8.9	11.3
101-H72								100	72			82	108	2,150	1,375	1,763	61.0	55.2	58.1	98.8	91.6	95.2	14.9	8.1	11.5
102-0	100	0	0	do				(2)		101.3	.0061	119	117	3,370	3,950	3,660				134.1	169.2	151.7	18.4	12.3	15.4
102-H24								100	24			114	112.5	2,040	1,990	2,015	60.5	50.4	55.5	175.2	152.8	164.0	18.0	11.4	14.7
102-H72								100	72			101	100	1,635	2,335	1,985	48.5	59.1	53.8	156.4	139.6	148.0	16.5	12.1	14.3
113-0	100	0	0	do	2.46	1.5	.51	(2)		66.1	.0040	66.2	100	3,900	5,595	4,748				116.8	134.8	125.8	11.0	8.6	9.8
113-H24								100	24			68.7	104	3,570	3,258	3,414	91.5	58.2	74.9	104.5	108.8	106.7	10.8	7.9	9.4
113-H48								100	48			65.6	99	2,619	3,200	2,909	67.2	57.2	62.2	107.2	114.4	110.8	10.5	7.9	9.2
113-H72								100	72			62.9	95	2,250	3,427	2,839	57.7	61.3	59.5	109.2	114.8	112.0	10.4	8.4	9.4
114-0	100	0	0	Rosin	0	1.4	.10	(2)		65.4	.0053	29.5	45	1,665	439	1,052				150.0	157.6	153.8	7.1	4.4	5.8
114-H24								100	24			32.2	49	1,759	425	1,092	106.0	96.8	101.4	152.0	147.2	149.6	7.2	4.4	5.8
114-H48								100	48			33.4	51	1,304	398	851	78.5	90.7	84.6	133.6	150.8	142.2	6.9	4.7	5.8
114-H72								100	72			32.9	50	1,333	341	837	80.3	77.7	79.0	132.4	126.4	129.4	7.1	4.8	5.9
118-0	100	0	0	Rosin and glue sizing.	4.65	1.6	.60	(2)		65.3	.0042	73.1	112	4,656	6,193	5,425				133.6	153.2	143.4	11.2	8.2	9.7
118-H24								100	24			70.4	108	3,214	4,479	3,847	68.9	72.4	70.7	119.2	126.0	122.6	10.9	8.0	9.5
118-H48								100	48			73.5	112	3,440	3,987	3,714	73.8	64.6	69.2	113.6	136.0	124.8	11.0	8.1	9.6
118-H72								100	72			66.6	101	2,550	3,398	2,974	54.7	55.0	54.9	102.8	117.6	110.2	11.0	7.9	9.5
119-0	100	0	0	Rosin	0	2.4	.54	(2)		67.1	.0054	42.5	63	2,557	1,668	2,113				143.2	149.6	146.4	9.1	5.1	7.1
119-H24								100	24			42.6	64	2,099	1,049	1,574	82.3	63.0	72.7	125.6	127.6	126.6	9.4	5.2	7.3
119-H48								100	48			42.6	64	915	799	857	35.8	48.0	41.9	99.2	105.6	102.4			
119-H72								100	72			41.2	61	534	370	452	20.9	22.2	21.6	89.6	95.6	92.6	8.7	5.5	7.1
120-0	100	0	0	Rosin and glue-sizing.	2.17	1.4	.73	(2)		66.4	.0053	69.0	104	3,639	2,814	3,227				152.0	132.8	142.4	11.3	7.4	9.4
120-H24								100	24			66.0	99	3,582	2,628	3,104	98.4	93.5	96.0	135.6	127.6	131.6	11.1	7.2	9.2
120-H48								100	48			67.1	102	2,578	2,524	2,551	70.8	89.8	80.3	121.2	120.4	120.8			
120-H72								100	72			65.5	99	2,593	2,601	2,597	71.1	92.5	81.8	117.6	115.6	116.6	10.4	7.1	8.8

[1] Approximately pounds per square inch.

[2] Control sample.

TEST ON ALL-RAG PAPERS—Continued

Sample No.	Fiber composition: Rag	Fiber composition: Coniferous wood	Fiber composition: Deciduous wood	Kind of sizing used	Chemical tests: Glue	Chemical tests: Resin	Ash	Aging test: Temperature	Aging test: Duration	Weight, 500 sheets 25 by 40 inches	Thickness	Bursting strength	Ratio bursting strength to weight	Folding endurance: Machine direction	Folding endurance: Cross direction	Folding endurance: Average	Folding endurance in per cent of initial: Machine direction	Folding endurance in per cent of initial: Cross direction	Folding endurance in per cent of initial: Average	Tearing strength: Machine direction	Tearing strength: Cross direction	Tearing strength: Average	Tensile strength: Machine direction	Tensile strength: Cross direction	Tensile strength: Average
	Per cent	*Per cent*	*Per cent*		*Per cent*	*Per cent*	*Per cent*	*° C.*	*Hours*	*Pounds*	*Inch*	*Points*[1]	*Per cent*	*Double folds*	*Double folds*	*Double folds*	*Per cent*	*Per cent*	*Per cent*	*g*	*g*	*g*	*kg*	*kg*	*kg*
127-0	100	0	0	Rosin	0	2.2	0.75	(2)		59.6	0.0039	51.6	87	3,337	1,246	2,292				112.0	108.4	110.2	9.4	5.5	7.5
127-H24								100	24			52.2	88	2,502	1,059	1,781	75.0	85.0	80.0	104.4	99.6	102.0			
127-H48								100	48			49.2	83	2,174	1,049	1,611	65.0	84.3	74.7	92.8	95.6	94.2			
127-H72								100	72			49.2	83	1,902	1,027	1,526	56.8	82.5	69.7	91.6	84.8	88.2	9.4	5.7	7.6
126-0	100	0	0	Rosin and glue-sizing.	4.64	2.3	.80	(2)		61.9	.0040	64.5	104	2,985	1,929	2,457				97.6	90.8	94.7	11.5	6.9	9.2
126-H24								100	24			65.1	105	2,804	1,854	2,129	80.4	96.2	88.3	91.2	86.8	89.0			
126-H48								100	48			65.4	107	2,652	1,746	2,199	88.7	90.5	89.6	86.4	84.8	85.6			
126-H72								100	72			63.4	103	2,206	1,541	1,873	73.8	79.8	76.8	85.6	84.8	85.2	11.5	6.6	9.1
129-0	100	0	0	Rosin	0	2.4	.71	(2)		60.3	.0038	48.1	80	3,117	2,606	2,862				135.2	140.0	137.6	8.8	5.7	7.3
129-H24								100	24			51.5	85	2,700	1,661	2,184	86.8	63.7	75.3	130.0	146.4	138.2			
129-H48								100	48			49.6	82	2,413	1,342	1,820	77.5	51.5	64.5	116.4	109.2	112.8			
129-H72								100	72			51.8	86	1,984	1,334	1,659	63.8	51.2	57.5	100.8	100.0	100.4	9.3	6.0	7.7
128-O	100	0	0	Rosin and glue sizing.	3.45	2.5	.77	(2)		65.2	.0040	69.2	106	3,499	2,628	3,063				124.8	117.6	121.2	11.3	6.2	8.8
128-H24								100	24			67.2	103	3,361	2,198	2,880	96.0	83.7	89.9	118.8	107.6	113.7			
128-H48								100	48			64.7	99	3,344	1,893	2,618	95.5	72.1	83.8	128.4	108.8	118.6			
128-H72								100	72			63.5	97	2,292	1,904	2,098	65.5	72.5	69.0	113.2	100.8	107.0	11.3	6.8	9.1
131-O	100	0	0	Rosin	0	1.7	.82	(2)		85.6	.0055	26.2	31	9.1	9.4	9.3				62.4	58.0	60.2	5.3	4.0	4.7
131-H24								100	24			25.8	30	6.3	7.2	6.8	69	77	73	65.2	61.2	63.2			
131-H48								100	48			25.1	29	5.1	7.5	6.3	56	80	68	62.4	61.6	62.0			
131-H72								100	72			25.2	29	5.5	6.7	6.1	60	65	63	58.8	64.8	61.8	5.6	4.3	5.0
130-O	100	0	0	Rosin and glue sizing.	3.44	1.5	.72	(2)		83.6	.0049	39.2	47	22	20	21				70.8	61.6	66.1	7.0	5.1	6.1
130-H24								100	24			39.5	47	20	16	18	91	80	86	67.6	65.2	66.4			
130-H48								100	48			37.6	45	10	20	15	45	100	73	70.0	68.4	69.2			
130-H72								100	72			37.6	45	8	14	11	36	70	53	70.0	66.4	68.2	7.2	5.5	6.4
121-O	100	0	0	Waterleaf	0	.09	.10	(2)		39.5	.0059	11.6	29	19.1	7.8	13.5				135.6	118.8	127.2	2.5	1.4	2.0
121-H72								100	72			11.9	30	24.2	7.1	15.9	127	91	109	119.8	110.4	125.6	2.4	1.4	1.9

[1] Approximately pounds per square inch.

[2] Control sample.

TEST ON PART-RAG PAPERS

[1] Approximately pounds per square inch.

[2] Control sample.

TEST ON PART-RAG PAPERS

103–O	95	5	0	Rosin and glue sizing.	6.72	1.8	1.22	[2]		64.4	0.0049	68	106	2,500	2,010	2,255				98.0	126.0	112.0	11.2	7.5	9.4
103–H24								100	24			69	106	1,860	1,265	1,563	74.5	63.0	68.8	97.6	98.0	97.8	11.0	7.3	9.2
103–H72								100	72			66	102	1,875	1,190	1,533	75.0	59.2	67.1	91.2	90.0	90.6	11.5	6.9	9.2
104–O	90	10	0	do	7.73	1.9	1.15	[2]		53.4	.0042	55	103	1,880	1,130	1,505				70.4	92.8	81.6	9.1	5.7	7.4
104–H24								100	24			53	99	1,345	570	958	71.6	50.2	60.9	68.8	78.0	73.4	8.5	5.2	7.9
104–H72								100	72			54	101	1,120	695	908	59.5	61.5	60.5	71.2	85.6	78.4	8.9	6.0	7.5
111–O	60	40	0	Rosin	0	2.7	.48	[2]		68.1	.0049	33.3	49	102	71	87				86.3	80.6	83.4	7.6	4.5	6.1
111–H24								100	24			31.5	46	41	46	44	40.2	64.8	52.5	78.3	79.1	78.7	7.8	4.3	6.1
111–H48								100	48			30.7	45	41	39	40	40.2	54.9	47.6	70.5	70.0	70.3	7.5	4.2	5.9
111–H72								100	72			30.2	44	16	23	20	15.7	32.4	24.1	62.8	59.4	61.1	7.3	4.4	5.9
112–O	60	40	0	Rosin and glue sizing.	1.05	2.5	.52	[2]		63.6	.0047	37.0	58	206	107	157				74.3	68.9	71.6	8.4	4.4	6.4
112–H24								100	24			34.8	55	59	39	49	28.7	36.5	32.6	64.3	62.3	63.3	8.4	4.5	6.5
112–H48								100	48			35.3	56	51	39	45	24.7	36.5	30.6	65.8	58.0	61.9	8.0	4.4	6.2
112–H72								100	72			31.0	49	18	24	21	8.7	22.4	15.6	56.3	49.4	52.8	7.8	4.1	6.0
133–O	65	35	0	Rosin	0	1.6	.39	[2]		64.3	.0048	41.7	65	337	191	264				75.6	68.0	71.8	8.6	4.9	6.8
133–H72								100	72			35.6	55	42	32	37	12.5	16.7	14.6	58.0	52.0	55.0	7.6	4.7	6.2
132–O	65	35	0	Rosin and glue sizing.	1.12	1.5	.43	[2]		64.4	.0046	47.4	74	339	172	256				69.2	67.2	68.2	9.0	5.4	7.2
132–H72								100	72			40.4	63	38	40	39	11.2	23.2	17.2	56.0	54.8	55.4	8.4	5.0	6.7

TESTS ON PURIFIED WOOD FIBER PAPERS

105–O	0	100	0	Rosin and glue sizing.	2.74	1.4	0.34	[2]		56.2	0.0039	44	78	1,420	800	1,110				78.4	86.4	82.4	8.2	5.1	6.7
105–H24								100	24			45	79	1,070	575	823	75.4	74.1	74.8	76.8	78.8	77.8	8.0	5.1	6.6
105–H72								100	72			43	77	655	495	575	46.9	61.9	54.4	65.2	70.4	67.8	8.1	5.1	6.6
106–O	0	100	0	do	2.36	1.5	.51	[2]		57.3	.0038	50	87	2,465	1,560	2,013				78.8	76.0	77.4	10.3	5.2	7.8
106–H24								100	24			49	85	1,585	1,265	1,425	64.3	81.0	72.7	80.8	71.2	76.0	9.7	4.7	7.2
106–H72								100	72			46	80	1,635	1,170	1,403	66.3	74.9	70.6	78.4	66.4	72.4	10.2	5.2	7.7
107–O	0	100	0	do	2.19	1.2	.39	[2]		69.3	.0046	58.7	85	1,855	1,180	1,518				112.8	98.8	105.8	11.4	5.3	8.4
107–H24								100	24			57.3	83	1,455	830	1,143	78.4	70.3	74.4	100.8	88.4	94.6	11.5	5.6	8.6
107–H48								100	48			57.1	83	1,450	880	1,165	78.2	74.5	76.4	95.6	86.0	90.8	11.9	5.5	8.7
107–H72								100	72			57.3	83	985	705	845	53.1	59.7	56.4	92.0	78.8	85.4	11.5	5.5	8.5
122–O	0	100	0	Waterleaf	0	.1	.15	[2]		36.6	.0037	15.8	43	83	6.7	44.8				65.8	50.2	58.0	4.1	1.3	2.7
122–H72								100	72			15.8	43	85	7.0	46.0	103	105	104	60.4	47.6	54.0	4.3	1.4	2.8

[2] Control sample.

TABLE 5.—*Test data on various artificially aged papers*—Continued

TESTS ON SULPHITE PAPERS

Sample No.	Fiber composition			Kind of sizing used	Chemical tests		Ash	Aging test		Weight, 500 sheets 25 by 40 inches	Thickness	Bursting strength	Ratio bursting strength to weight	Folding endurance			Folding endurance in per cent of initial			Tearing strength			Tensile strength		
	Rag	Coniferous wood	Deciduous wood		Glue	Resin		Temperature	Duration					Machine direction	Cross direction	Average	Machine direction	Cross direction	Average	Machine direction	Cross direction	Average	Machine direction	Cross direction	Average
	Per cent	*Per cent*	*Per cent*		*Per cent*	*Per cent*	*Per cent*	*° C.*	*Hours*	*Pounds*	*Inch*	*Points*[1]	*Per cent*	*Double folds*	*Double folds*	*Double folds*	*Per cent*	*Per cent*	*Per cent*	*g*	*g*	*g*	*kg*	*kg*	*kg*
108–0	0	100	0	Rosin	0	2.2	7.12	(2)		64.6	0.0039	24.9	39	15	17	16				50.4	48.8	49.6	6.7	3.0	4.9
108–H24								100	24			22.5	35	4	7	6	27	41	34	42.7	37.1	39.9	7.4	3.2	5.3
108–H48								100	48			21.5	33	2	3	3	13	18	16	37.3	33.4	35.4	7.3	3.4	5.4
108–H72								100	72			20.1	31	1	2	2	7	12	10	37.7	35.1	36.4	7.3	3.3	5.3
109–0	0	100	0	do	0	2.4	1.06	(2)		64.3	.0050	27.0	42	49	22	36				67.2	61.2	64.2	7.6	3.0	5.3
109–H24								100	24			22.8	35	13	11	12	27	50	39	55.9	46.2	51.1	7.5	3.0	5.3
109–H48								100	48			22.4	35	3	4	4	6	18	12	51.7	43.7	47.7	7.3	3.1	5.2
109–H72								100	72			21.0	31	2	3	3	4	14	9	45.1	40.0	42.6	7.1	3.2	5.2
110–0	0	100	0	do	0	2.8	.60	(2)		53.3	.0037	33.6	63	529	249	389				59.4	50.0	54.7	8.6	4.6	6.6
110–H24								100	24			29.3	55	17	30	24	3	12	8	40.3	34.3	37.3	8.0	4.4	6.2
110–H48								100	48			26.2	49	7	12	10	1	5	3	38.7	31.5	35.1	7.4	4.3	5.9
110–H72								100	72			23.3	44	5	2	4	1	1	1	30.0	27.1	28.6	7.0	4.2	5.6
115–0	0	100	0	do	0	1.3	2.61	(2)		43.3	.0032	24.7	57	135	130	133				40.8	42.4	41.6	6.5	3.5	5.0
115–H24								100	24			21.3	49	25	40	33	18	31	25	34.3	33.7	34.0	5.6	3.1	4.4
115–H48								100	48			19.3	45	16	28	22	10	21	16	30.6	29.4	30.0	5.5	3.0	4.3
115–H72								100	72			20.2	47	12	28	20	9	21	15	29.1	28.8	29.0	5.8	3.1	4.5
116–0	0	100	0	do	0	1.9	.51	(2)		65.8	.0043	36.9	56	501	364	433				76.8	73.2	75.0	9.5	5.1	7.3
116–H24								100	24			32.8	50	32	67	50	6	18	12	58.0	52.6	55.3	9.0	4.9	7.0
116–H48								100	48			30.0	46	4	17	11	1	5	3	48.6	44.0	46.3	9.0	4.7	6.8
116–H72								100	72			29.2	44	3	17	10	1	5	3	45.4	42.0	43.7	9.2	4.9	7.1
117–0	0	100	0	do	0	1.4	2.92	(2)		55.1	.0038	30.6	56	150	157	154				49.1	55.5	52.3	7.8	4.2	6.0
117–H24								100	24			28.0	51	30	62	46	20	40	30	41.4	47.1	44.3	7.6	4.1	5.9
117–H48								100	48			26.9	49	12	32	22	8	20	14	37.1	40.8	39.0	6.9	4.3	5.6
117–H72								100	72			25.4	46	10	27	19	7	17	12	40.9	40.0	40.5	7.3	3.8	5.6
134–0	0	100	0	do	0	1.7	.48	(2)		64.6	.0047	38.1	59	510	191	351				80.0	73.2	76.6	9.0	4.7	6.9
134–H72								100	72			27.7	43	1	46	3.8									

134–0	0	100	0	do	0	1.7	.48	[2]	72	64.6	.0047	38.1	59	510	191	351				80.0	73.2	76.6	9.0	4.7	6.9
134–H72								100				27.7	43	1	46	2.8	.2	2.4	1.3	35.2	32.8	34.0	6.9	4.0	5.5
135–0	0	100	0	do	0	2.0	6.12	[2]	72	64.6	.0040	27.3	42	106	72	89				62.4	52.4	57.4	7.2	3.3	5.3
135–H72								100				23.4	36	4.9	5.8	5.4	4.6	8.1	6.4	44.8	37.2	41.0	6.7	3.2	5.0

TESTS ON SODA-SULPHITE PAPERS

123–0	[3]	65	35	Rosin	0	0.6	19.11	[2]	72	49.8	0.0033	16.1	32	4.8	4.0	4.4				43.2	40.8	42.0	4.6	2.5	3.6
123–H72								100				15.0	30	1.4	1.6	1.5	29	40	35	35.6	33.2	34.4	4.7	2.5	3.6
124–0	[3]	50	50	do	0	.8	19.99	[2]	72	65.9	.0054	13.4	20	2.4	1.9	2.2				52.2	53.2	52.7	4.3	2.3	3.3
124–H72								100				12.3	19	1.0	1.0	1.0	42	53	48	47.0	45.0	46.0	4.2	2.1	3.2
147–0	0	35	65	do	0	.6	17.25	[2]	72	61.2	.0034	20.7	34	15.7	5.6	10.7				41.2	33.6	37.4	5.8	2.8	4.3
147–H72								100				19.6	32	9.2	3.9	6.6	59	70	64	44.4	32.4	38.4	5.5	2.7	4.1
148–0	0	75	25	do	0	1.9	5.04	[2]	72	66.2	.0052	19.4	29	15.3	7.6	11.5				66.4	58.8	62.6	4.9	2.4	3.7
148–H72								100				18.5	28	3.6	3.7	3.7	24	49	37	36.4	55.6	46.0	4.7	2.4	3.6
152–0	0	25	75	do	0	1.1	15.55	[2]	72	59.1	.0040	20.1	34	8.9	6.5	7.7				41.2	39.2	40.2	5.9	3.1	4.5
152–H72								100				19.6	33	5.6	4.9	5.3	63	75	69	39.6	36.4	38.0	5.7	3.2	4.5

[1] Approximately pounds per square inch.

[2] Control sample.

[3] Trace.

The folding endurance is generally considered to be the most valuable of the above tests in judging the probable durability or resistance of a paper to continued handling. Not only is the test indicative, in a general way, of the distinctive qualities of fibers in the papers, but the remarkable sensitivity of this test to heat or other arbitrary aging tests makes it a valuable means of classifying papers as to their probable permanence. Apart from the important effect of the quality of the basic fibers on the folding endurance of papers, the test is also influenced, in large part, by the treatment given the fiber. By referring to Table 5 it may be seen that the sulphite papers there represented vary from a few folds up to nearly 500 folds, although the variations in qualities of the pulps used for these papers were probably relatively slight. Among the rag papers even greater variations in folding endurance occur because of a greater variance among the factors affecting this test, which, aside from quality and purity of basic fiber, are treatment in the beater, method of sizing, quality of sizing materials, method of drying paper, etc.

The tearing test is probably more influenced by the strength of fibers in the paper than any of the other tests. On referring to the tests made on papers before and after being surface sized with glue, it will be observed that while the folding endurance, bursting, and tensile strength are all increased materially by the glue the tearing strength is not. The tearing test is of further interest in this work because of its sensitivity to the aging test. Artificially-aged papers decrease in tearing strength very sharply on being heated for 72 hours at 100° C., although not to the same extent to which they do in folding endurance. It is interesting to note that a fair degree of correlation exists between the decrease in folding and the decrease in tearing strength resulting from the aging test.

Neither the bursting strength nor the tensile strength of papers is markedly affected by the heat treatment, except in cases where the papers are conspicuously of impermanent character or, in some cases, where the values may be said to be fictitious, in a sense, due to an abnormal amount of strength imparted by glue sizing.

(2) Discussion of Accelerated Aging Tests.—As a result of preliminary investigations of several types of accelerated aging tests, the usual one was found to be satisfactory and, in general, the most convenient. This test consists in placing the sample in an oven maintained at 100° C. for a given length of time. In Table 5 strength values are given for papers which have been subjected to the heat test for 24, 48, and 72 hours. The effect of varying the duration of heat treatment on folding endurance is expressed graphically in Figures 8, 9, and 10 as per cent of initial folding endurance retained at the end of each period of exposure. A study of the curves indicates that a 72-hour period of heating is probably more desirable than a

shorter period. At the end of 24 hours of heating the sharpest decrease in folding endurance takes place, especially among the less permanent types of papers, but reaches a more constant value between 48 and 72 hours. Therefore, the per cent of initial folding endurance

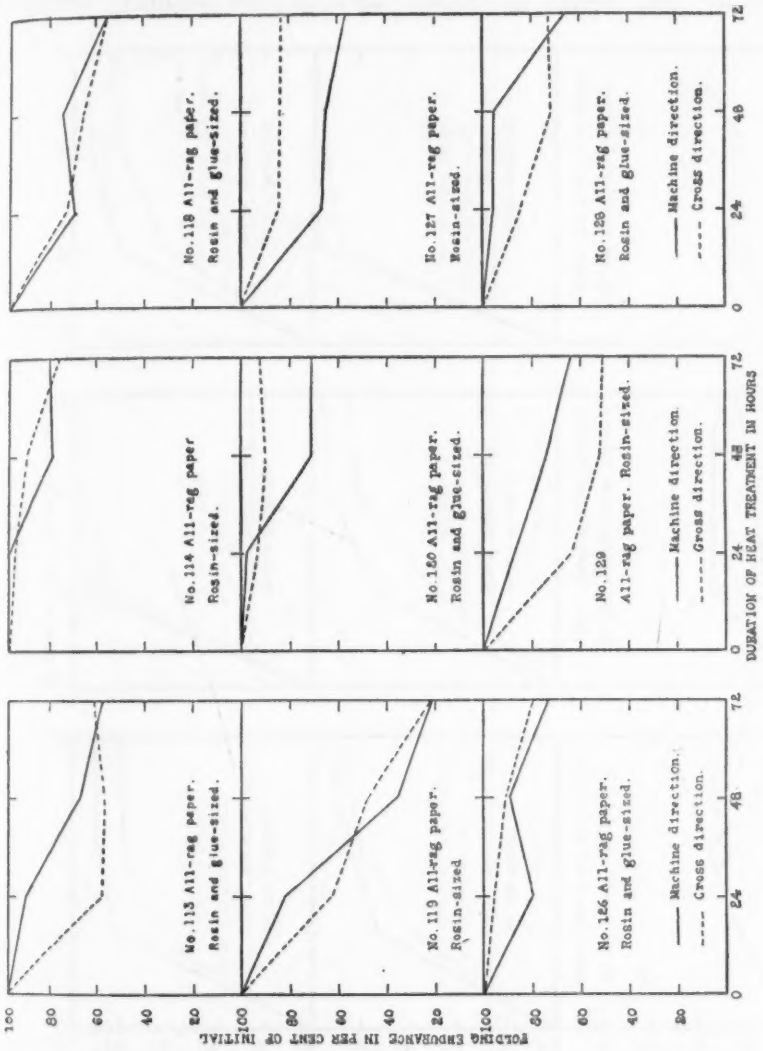
No. 118 All-rag paper. Rosin and glue-sized.
No. 127 All-rag paper. Rosin-sized.
No. 126 All-rag paper. Rosin and glue-sized.
No. 114 All-rag paper Rosin-sized.
No. 120 All-rag paper. Rosin and glue-sized.
No. 129 All-rag paper. Rosin-sized.
No. 113 All-rag paper. Rosin and glue-sized.
No. 119 All-rag paper. Rosin-sized
No. 125 All-rag paper. Rosin and glue-sized.
Machine direction.
Cross direction.
DURATION OF HEAT TREATMENT IN HOURS
FOLDING ENDURANCE IN PER CENT OF INITIAL

FIGURE 8

retained after a heat treatment of 72 hours at 100° C. is considered the "permanency factor" of a given paper.

Another type of accelerated aging test, in which papers were exposed to a temperature of 95° C. for 72 hours in an atmosphere of humidified air, was tried for different types of papers. Except for being somewhat less drastic than the latter, the relative effects were the same, and therefore the test was abandoned.

A third type of aging test that was tried consisted in exposing the sample to the action of steam at atmospheric pressure for two hours. This treatment was found to be sufficient to cause a considerable reversion in the colors of the papers. It was found to be difficult to reproduce test results on papers aged in this manner, probably

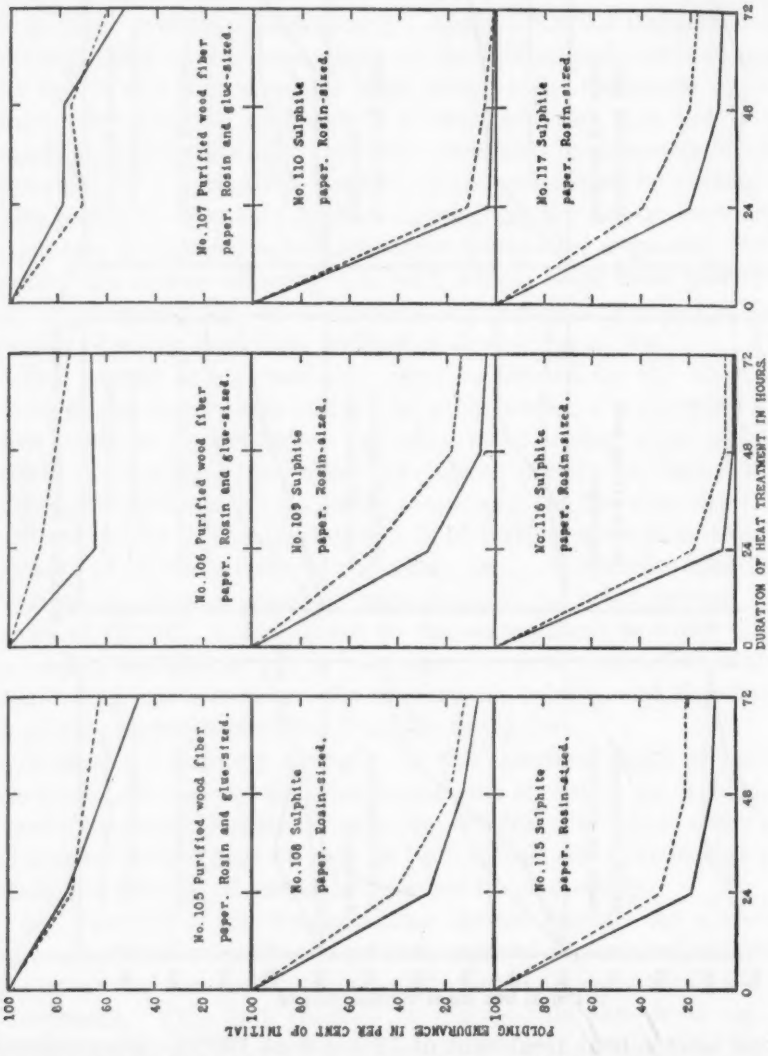
No. 107 Purified wood fiber paper. Rosin and glue-sized.
No. 110 Sulphite paper. Rosin-sized.
No. 117 Sulphite paper. Rosin-sized.
No. 106 Purified wood fiber paper. Rosin and glue-sized.
No. 109 Sulphite paper. Rosin-sized.
No. 116 Sulphite paper. Rosin-sized.
No. 105 Purified wood fiber paper. Rosin and glue-sized.
No. 108 Sulphite paper. Rosin-sized.
No. 115 Sulphite paper. Rosin-sized.
FOLDING ENDURANCE IN PER CENT OF INITIAL
DURATION OF HEAT TREATMENT IN HOURS.
0
24
48
72
100
80
60
40
20

FIGURE 9

because of the fact that any condensate unavoidably dropping on the sheet, thus moistening it, would tend to give higher strength values. Glue-sized papers of all types decrease in folding endurance to about the same extent as a result of the steam exposure to which they do when heated in dry air at 100° C. for 72 hours. Rosin-sized papers having no surface sizing of glue appear to be relatively much less

affected. Similar steam treatments made on paper-making fibers of all types caused no decrease in the alpha cellulose of even the most impermanent of the fibers; therefore, it is probable that this type of artificial aging does not simulate the effects of natural aging nearly so closely as the ordinary heat test first considered.

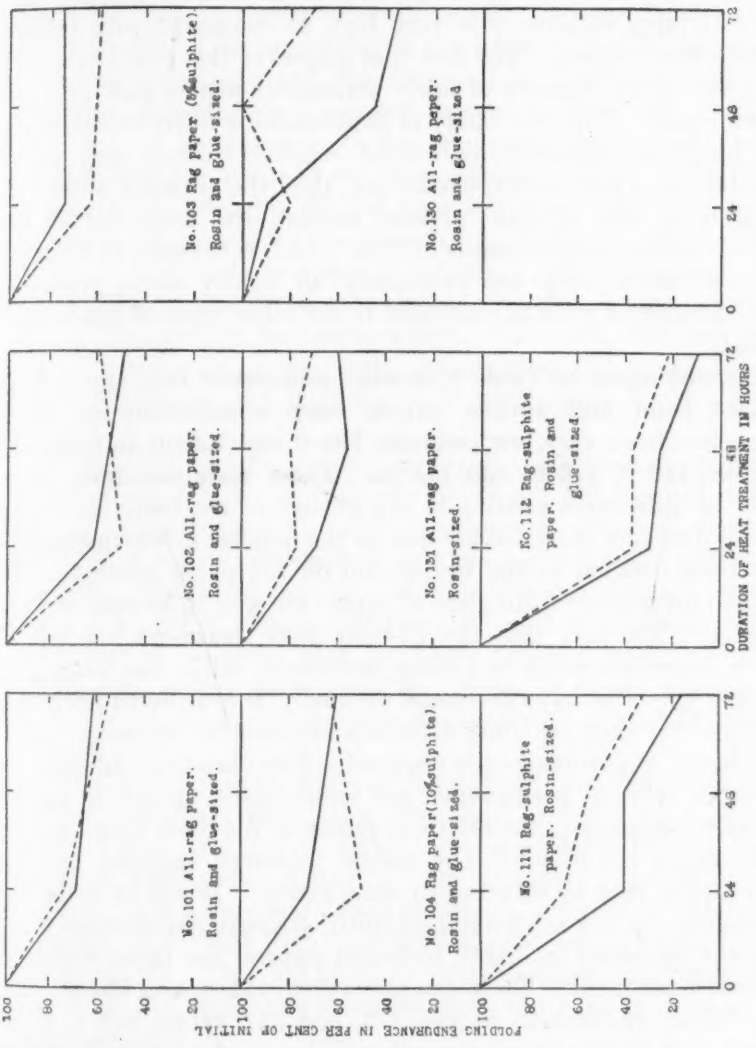
No. 103 Rag paper (½ sulphite). Rosin and glue-sized.
No. 130 All-rag paper. Rosin and glue-sized
No. 102 All-rag paper. Rosin and glue-sized.
No. 131 All-rag paper. Rosin-sized.
No. 112 Rag-sulphite paper. Rosin and glue-sized.
No. 101 All-rag paper. Rosin and glue-sized.
No. 104 Rag paper (10% sulphite). Rosin and glue-sized.
No. 111 Rag-sulphite paper. Rosin-sized.
0
24
48
72
DURATION OF HEAT TREATMENT IN HOURS
100
80
60
40
20
FOLDING ENDURANCE IN PER CENT OF INITIAL

FIGURE 10

(3) DETAILED DISCUSSION OF RESULTS OBTAINED WITH VARIOUS PAPERS.—The book papers made from mixtures of soda pulps and sulphite pulps are considerably different from the other types of papers studied in that they have been made more with regard to printing qualities than for high strength or durability. They were included in this investigation for the purpose of learning more about

the particular properties imparted to papers by the soda-pulp fiber. The test results given in Table 5 show that, while these papers are characterized by relatively very poor strength properties, they show a surprising resistance to the effects of artificial aging on these properties. In all cases the bursting, tearing, and tensile strengths are not altered to any marked degree by the heat treatment, and the retention of folding endurance is very high as compared with ordinary sulphite bond papers. The fact that papers of this type react to the aging test in the manner of fairly permanent papers may be due to several causes: First, the study of paper-making fibers indicated that soda pulps of sufficiently high alpha cellulose content may be considerably more permanent, chemically, than the ordinary wood fibers prepared by the sulphite process; second, the book papers here studied contain large amounts of filler, which is thought to favor permanency; third, they are practically all lightly sized, containing small amounts of rosin as compared to the other types of papers being studied.

Referring again to Table 5, it will be observed that the ordinary sulphite bond and writing papers vary considerably in folding endurance, from very low (samples 108–0 and 109–0) to fairly high (samples 110–0, 116–0, and 134–0). These variations may be due partly to differences existing in the quality of the basic fibers used, but are probably more largely due to the manner in which the fibers have been handled in the beater and on the paper machine. The strength properties of this class of papers are seen to be very sensitive to aging. The fact that the 72-hour heat treatment has left the papers extremely weak in folding endurance, while the tearing and bursting strengths have decreased decidedly, is considered fairly good evidence that they are quite definitely unsuited for purposes where a high degree of permanence is required. The variations among these papers in relative permanence are undoubtedly caused in part by differences existing in the chemical purity of the basic fibers and also unlike sizing conditions. The results, however, indicate that two other factors may be involved to some extent. It will be noted that the samples having relatively high initial strength characterisics, such as might be found in highly hydrated papers, are those which are the least permanent. Thus, samples 110–0, 116–0, and 134–0, which have folding endurances of 389, 433, and 351, retain but 1, 3, and 1.3 per cent of this initial fold after 72 hours of heating at 100° C. On the other hand, samples 108–0 and 109–0, of markedly low original folding endurance, retain 10 and 9 per cent after the aging test. Although excessive hydration is considered a probable cause of deterioration, the presence of filler in the paper appears to have a beneficial effect. The papers containing filler, indicated by high ash

content, all seem to be more resistant to the aging test than other papers containing no filler.

Three purified wood-fiber papers, surface sized with glue and otherwise prepared in a manner similar to high-grade rag papers, were available for this study. All these samples are characterized by very high strength qualities and in every respect appear to be entirely distinct in character from papers prepared from ordinary sulphite fibers. This superiority is particularly marked in regard to the folding endurance and the retention of this quality after the aging test. Sample 106–0 appears to combine best the qualities of durability and permanence, having an initial folding endurance of over 2,000 and losing but 29 per cent of this as a result of the 72-hour heat treatment. Sample 122 is a waterleaf paper made from purified wood fiber, and is used for the preparation of cellulose esters. It was included in this study in order to determine the permanence of this type of fiber when no sizing materials or other foreign substances affecting permanence had been added. The fact that the folding endurance suffers no appreciable change after the paper has been heated indicates a very high degree of permanence for this type of fiber.

The so-called part-rag papers consist of rag fiber and appreciable amounts of sulphite pulp. Samples 103–0 and 104–0, while included under this classification in Table 5 because of the small amount of sulphite fiber which they contain, are not representative of this class of papers. The wood fiber probably entered as "broke" into the beater. The other papers containing 35 and 40 per cent sulphite pulp appear to be made with rag fibers that are relatively poor in strength and permanence qualities. None of these latter papers appears to be markedly superior to the better grades of ordinary sulphite bonds.

A considerable variety of all-rag papers were available for study and with few exceptions they have very good strength characteristics. Samples 130–0 and 131–0, which are particularly poor in folding endurance, were prepared from a "No. 1 white" grade of old rags. Sample 121–0 is a waterleaf paper, the fiber of which was undoubtedly not beaten to develop strength qualities, used for the preparation of cellulose esters. The fact that its initial folding endurance is not affected by the aging test indicates that the basic fiber is of very high permanence.

The number of rag papers sampled before and after the size tub affords an opportunity to study the effect of glue sizing on the various properties of papers. Referring to Table 5, it will be seen that the glue has increased the bursting and tensile strengths substantially, and the folding endurance to a widely varying extent and has decreased the tearing strength somewhat.

It is indicated that when considerable strength has been imparted to paper by tub-sizing with glue, this added strength may be quite largely lost when the paper is heated. This decrease in strength may not be evidence of any great change in the strength of the basic fibers composing the sheet, nor does it necessarily indicate correspondingly poor permanence qualities for the paper. Samples 101–0, 102–0, and 118–0 all have high glue contents. It can not be stated just how much of the initial strength of samples 101–0 and 102–0 results from the use of glue sizing, since the corresponding unsized papers were not available. That considerable folding endurance has been imparted to sample 118–0 by the use of glue is known because its folding endurance is about fivefold that of the unsized paper corresponding to it, sample 114–0. It will be noted that the latter retained 79.0 per cent of its initial folding endurance on being heated 72 hours at 100° C., while the glue-sized paper retained but 54.9 per cent. Also, samples 101–0 and 102–0 have decreased in folding endurance somewhat more rapidly than other papers of this type generally do. Even the bursting and tensile strengths undergo appreciable changes on heating, which is unusual for the more permanent papers.

In the case of other papers studied, however, where glue sizing has not increased the folding endurance to any great extent, the decrease in folding endurance caused by heating is usually somewhat greater for the unsized than for the sized paper. Samples 126–0 and 128–0 represent papers having folding endurance substantially the same as the unsized papers corresponding to them, 127–0 and 129–0. The per cent retention of folding endurance after heating 72 hours at 100° C. is 76.8 and 69.0 for the glue-sized papers, as against 69.7 and 57.5 for the corresponding unsized papers. There is some indication here that the glue helps protect the fiber from deterioration. Later on evidence is offered to show that glue tub sizing does help to retard chemical degradation.

In Figure 11 is given a graphical representation of the comparative permanence of different types of papers, as determined by the per cent retention of folding endurance after the standard heat treatment of 72 hours at 100° C. The purified wood fiber papers re-act to the aging test in much the same manner as the high-grade rag papers, and therefore it can reasonably be assumed that the resistance of these papers to the deterioration caused by natural aging would be of the same order. A comparison of the two types of papers from the standpoint of strength qualities or durability is made difficult because of the fact that only a limited number of purified wood fiber papers were available. While some of the rag papers test considerably higher in tearing strength and folding endurance, it can not be stated definitely, from the results tabulated, just how optimum papers prepared from the two fibers would compare.

(b) COLOR CHARACTERISTICS

The color characteristics of the various papers reported in Table 6 are seen to have been markedly influenced by the color properties of the fibers from which these papers were made. In the study of wood pulps and rag half stocks, it was found that the sulphite pulps reverted the most in color as a result of the 72-hour heat treatment at 100° C. Similarly, the papers prepared from sulphite pulps are the most susceptible to reversion in color; both in respect to decrease in total brightness and in departure from true white, which latter character-

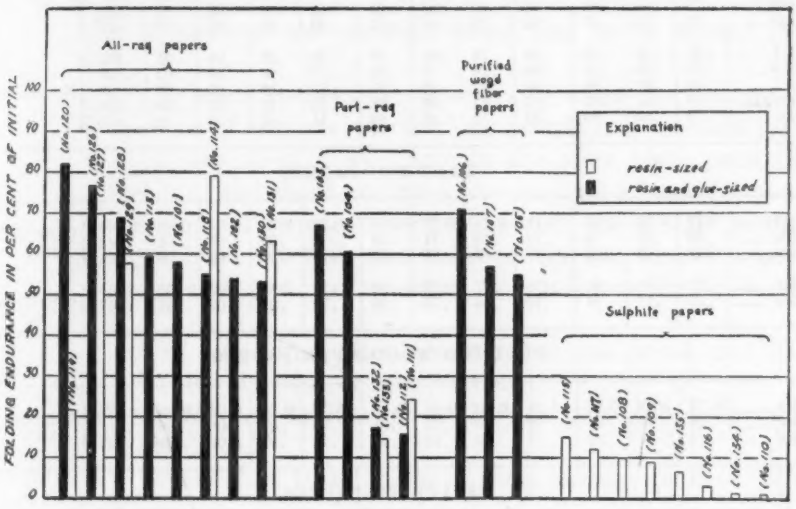

FIGURE 11

istic manifests itself as a relative increase in the predominating tint—red. Next in order of susceptibility to reversion in color are the papers prepared from mixtures of sulphite pulps and rag fibers; then follow the book papers prepared from mixtures of sulphite pulps and soda pulps; and, finally, purified wood fiber papers and high-grade rag papers, which latter two appear to be about equal in color stability. In general, it is evident that papers which are impermanent in chemical or physical properties will also tend to discolor readily. Considering the sulphite papers alone, it is apparent that the three showing marked impermanence in regard to loss of physical strength after aging stand out as the papers reverting most in color.

TABLE 6.—*Color stability of various commercial papers*

Sample No.	Brightness value of control sample				Brightness value of sample heated at 100° C. for 72 hours				Decrease in brightness values due to heating				Remarks
	Blue	Green	Red	Total brightness [1]	Blue	Green	Red	Total brightness [1]	Blue	Green	Red	Total decrease [2]	
ALL-RAG PAPERS													
113	0.72	0.84	0.89	0.82	0.67	0.81	0.88	0.79	0.05	0.03	0.01	0.030	Rosin and glue sized.
118	.71	.78	.85	.78	.66	.74	.82	.74	.05	.04	.03	.040	
120	.75	.81	.86	.81	.71	.78	.85	.78	.04	.03	.01	.027	
126	.75	.84	.89	.83	.72	.83	.89	.81	.03	.01	.00	.013	
128	.75	.85	.90	.83	.69	.83	.89	.80	.06	.02	.01	.030	
130	.76	.83	.87	.82	.73	.81	.87	.80	.03	.02	.00	.017	
114	.81	.86	.92	.86	.78	.85	.91	.85	.03	.01	.01	.017	Rosin sized.
119	.73	.79	.84	.86	.68	.75	.82	.75	.05	.04	.02	.037	
127	.78	.87	.91	.85	.72	.86	.91	.83	.06	.01	.00	.023	
129	.78	.87	.91	.85	.73	.86	.91	.83	.05	.01	.00	.020	
131	.79	.85	.89	.84	.72	.83	.89	.81	.07	.02	.00	.030	
PART-RAG PAPERS													
112	0.72	0.74	0.82	0.76	0.64	0.72	0.80	0.72	0.08	0.02	0.02	0.040	Rosin and glue sized.
132	.69	.74	.79	.74	.60	.71	.78	.70	.09	.03	.01	.043	
104	.72	.78	.82	.77	.67	.76	.82	.75	.05	.02	.00	.023	
111	.71	.75	.80	.75	.61	.73	.80	.73	.10	.02	.00	.040	Rosin sized.
133	.73	.77	.81	.77	.64	.73	.80	.72	.09	.04	.01	.047	
PURIFIED WOOD-FIBER PAPERS													
105	0.75	0.82	0.86	0.81	0.70	0.80	0.86	0.79	0.05	0.02	0.00	0.023	Rosin and glue sized.
106	.71	.76	.81	.76	.68	.75	.81	.75	.03	.01	.00	.013	
107	.73	.77	.82	.77	.70	.75	.81	.75	.03	.02	.01	.020	
SULPHITE PAPERS													
108	0.75	0.80	0.84	0.80	0.66	0.76	0.83	0.75	0.09	0.04	0.01	0.047	Rosin sized.
109	.73	.79	.84	.79	.64	.75	.83	.74	.09	.04	.01	.047	
110	.73	.77	.82	.77	.61	.71	.80	.71	.12	.06	.02	.067	
115	.70	.77	.83	.77	.65	.74	.82	.74	.05	.03	.01	.030	
116	.71	.76	.81	.76	.60	.72	.80	.71	.11	.04	.01	.053	
117	.72	.78	.83	.78	.63	.77	.83	.74	.09	.01	.00	.033	
135	.75	.86	.90	.84	.68	.79	.88	.77	.10	.07	.02	.063	
SODA-SULPHITE PAPERS													
123	0.74	0.82	0.87	0.81	0.69	0.80	0.87	0.79	0.05	0.02	0.00	0.023	Rosin sized.
124	.75	.84	.89	.83	.72	.83	.89	.81	.03	.01	.00	.013	
147	.68	.74	.83	.75	.61	.72	.82	.72	.07	.02	.01	.033	
148	.69	.77	.86	.77	.61	.74	.85	.73	.08	.03	.01	.040	
152	.65	.79	.87	.77	.61	.77	.87	.75	.04	.02	.00	.020	

[1] Approximate brightness for white light.
[2] Decrease in approximate brightness for white light.

Another effect apparent in the color characteristics of the papers may be mentioned. Referring to the results obtained for rag papers, it will be observed that the glue-sized papers tend to be more sensitive to color changes than similar papers sampled before tub sizing.

(c) ERASING QUALITY OF BOND PAPERS MADE FROM RAG FIBERS AND FROM PURIFIED WOOD FIBERS

Tests were made of the erasing quality of rag papers as compared with that of certain purified wood-fiber papers. In order to obtain some preliminary information on this subject, two papers prepared from the highest grade of rag half stock were subjected to erasure tests and compared, in this respect, with three available papers prepared from purified wood fibers. All papers were rosin and glue sized and contained approximately the same amounts of these sizing materials. A description of the test procedure used follows.

Straight lines were drawn with a ruling pen with standard testing ink, making a more or less average width line as in normal pen writing.

The quality of each consecutive line drawn after the erasure of the middle portion of the original line was noted; and the sum total of the repeated erasure of lines drawn in the same place until the rubbing through of the sheet occurred was used as a basis for comparison of samples. The reason for erasing only the middle portion of each line is to leave the ends as a guide for the new line after each erasure. The above test was checked for each sample to insure accuracy.

The surface of the paper after erasure also was noted and had some bearing on the decision of relative merits.

The faults noted were feathering of the pen lines and a skipping of the ink on the lines.

All of the papers were found to have good erasing quality. The test data are given in Table 7 in order of the relative ranking of the papers in respect to resistance to erasing, No. 113 being considered the best and No. 120 the poorest.

TABLE 7.—*Erasure tests* [1]

Sample No.	Description	Weight, 500 sheets 25 by 40 inches	Rosin	Glue
		Pounds	*Per cent*	*Per cent*
113	100 per cent rag bond. Rosin and glue sized	66.1	1.53	2.46
107	100 per cent purified wood fiber bond paper. Rosin and glue sized	69.3	1.24	2.19
106	do	57.3	1.53	2.36
105	do	56.2	1.41	2.74
120	100 per cent rag bond. Rosin and glue sized	66.4	1.35	2.17

[1] Papers are arranged in order of their erasure qualities, No. 113 being considered the best.

The data indicate that high-grade rag papers and papers prepared from purified wood fibers withstand erasure to about the same extent. The probabilities are that fiber composition has only a minor influence on this particular quality of paper and that other factors entering

into its manufacture (for example, quality and amount of sizing materials and treatment of fibers in the beater) have a much more important effect.

(d) ALPHA CELLULOSE CONTENT

The effect of the artificial aging test on the alpha cellulose content of some typical papers is given in Table 8. Referring to Table 5, it is evident that there is a correlation between the decrease in folding endurance and the decrease in alpha cellulose content. For example, the sulphite papers and those prepared from mixtures of sulphite pulp and rags, which dropped markedly in folding endurance when heated for 72 hours at 100° C., revealed a corresponding instability in alpha cellulose content; on the other hand, the purified wood-fiber papers and all-rag papers of relatively good permanence lost less than 2 per cent. To illustrate the effect on an all-rag paper of poor permanence, sample 119–O, which retained but 21.6 per cent of its initial folding endurance after the heat treatment, dropped 6.0 per cent in alpha cellulose. It may be noted that the surface-sized papers are more stable in this respect than similar papers sampled before tub sizing, suggesting, as was indicated before, that the surface coating of glue may actually assist the aging qualities of a paper.

TABLE 8.—*Decrease in alpha cellulose content of papers on heating for 72 hours at 100° C.*

Sample No.	Alpha cellulose content		
	Control sample	Sample heated 72 hours at 100° C.	Amount of initial alpha cellulose lost
	Per cent	*Per cent*	*Per cent*
ALL-RAG PAPERS			
119	90.7	85.2	6.0
120	91.0	89.7	1.4
114	97.5	96.5	1.0
118	89.1	88.6	.6
PART-RAG PAPERS			
111	79.8	73.6	7.8
112	78.9	73.9	6.3
133	77.7	73.3	5.7
132	78.1	74.4	4.7
PURIFIED WOOD-FIBER PAPERS			
105	86.8	85.8	1.1
106	85.3	83.7	1.9
107	85.3	83.7	1.9
SULPHITE PAPERS			
108	76.1	71.8	5.7
110	79.3	74.6	5.9

VI. FURTHER WORK

1. A method is very much needed for identifying purified wood fibers in papers. A satisfactory estimation of the purified fibers in the presence of sulphite fibers can not be readily made by means of any of the stains commonly used in fiber-analysis work. An attempt is being made to devise some stain which will differentiate these fibers.

2. It has been noted that the nonalpha cellulose constituents of different types of fibers vary, weight for weight, in the extent to which they influence deterioration. It is indicated that certain substances such as pentosans are comparatively inert, while the modified celluloses are very active in causing further degradation. It is proposed to study further the relative effects of these different impurities.

3. A considerable amount of preliminary work has been done, indicating that the fluidity in cupra-ammonium solution may offer a ready means of measuring important qualities in paper-making fibers. Further work is planned to correlate such data with data on the strength and permanence qualities of papers.

4. With the results of the investigation of commercial papers and paper-making fibers as a basis, the plan of work will finally include a study of a series of papers prepared in the Bureau of Standards paper mill, in order to establish more conclusively the relative paper-making qualities of the different types of fibers. This work will involve the preparation from each type of material under consideration the best possible quality of paper, in which have been eliminated, as far as possible, most of the variables entering unavoidably into the manufacture of papers at different mills.

5. Before concluding the work on the present series of commercial papers additional samples will be tested for alpha cellulose content, copper number, and acidity. The effect of artificial aging on these properties will also be determined.

VII. SUMMARY AND CONCLUSIONS

The qualities of purified wood fibers and commercial papers prepared from these fibers have been investigated from the standpoint of chemical purity, color, durability, and permanence.

The data obtained thus far point to the following general conclusions:

1. While it is desirable that the alpha cellulose content of paper-making fibers intended for permanent uses should be as high as possible, conclusions based on this determination alone may be in error due to the fact that the nonalpha cellulose constituents of different types of fibers vary, weight for weight, in the extent to which they influence the permanence qualities of these fibers. Modified celluloses are

known to be active in causing rapid deterioration of cellulose; pentosans, on the other hand, appear to be relatively inert in this respect.

2. The decrease in the alpha cellulose content of a material, caused by artificial aging, is considered an indication of relative permanence. Purified wood fibers, like purified rag fibers, undergo but slight loss of alpha cellulose after an exposure to an accelerated aging test (100° C. for 72 hours).

3. Changes in the alpha cellulose content of papers brought about by artificial aging are accompanied by fairly proportionate changes in physical properties, such as folding endurance and tearing strength.

4. Purified wood fibers, like purified rag fibers, have excellent color characteristics. Since they are relatively very resistant to the effects of artificial aging, it is indicated that they would show similar good resistance to the yellowing effects of natural aging.

5. A high degree of hydration appears to be detrimental to the permanence of a paper.

6. Inert mineral fillers may be safely added to furnishes for permanent papers and probably aid to some extent in preventing deterioration.

7. The increased strength imparted to papers by glue tub-sizing is rapidly lost on heating, despite the fact that such sizing apparently increases the permanence of papers. Evidently the glue functions as a protective surface, retarding chemical deterioration. Starch, which is also commonly used for the tub-sizing of papers, possibly reacts in a manner similar to glue, but there were not a sufficient number of starch-sized papers included in these tests to permit a definite conclusion in this respect.

8. The manner in which the purified wood fibers, and papers prepared from them, react to the various tests which have been applied indicates that they are well adapted for use in high-quality bond and permanent record papers, which have hitherto been made exclusively from furnishes of high-grade rag half stock. It is hoped that the further researches in progress will lead to more definite conclusions in this respect.

WASHINGTON, February 16, 1929.

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